

SYNTHESIS AND PHYSICO - CHEMICAL STUDIES OF
PHTHALEINS AND SUCCINEINS WITH A CHIRAL
CARBON ATOM

THESIS

SUBMITTED FOR THE DEGREE OF

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IN CHEMISTRY

OF

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Supervisor

Dr. I. M. BEG

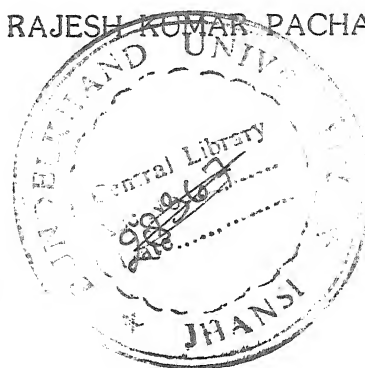
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By

RAJESH KUMAR PACHAURI



1993

CERTIFICATE

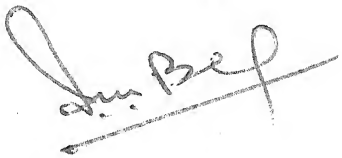
This is to certify that the work presented in this thesis, entitled, "SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF PHTHALEINS AND SUCCINEINS WITH A CHIRAL CARBON ATOM", was carried out under my guidance by the candidate, Mr. Rajesh Kumar Pachauri, personally for the degree of Doctor of Philosophy in Chemistry of this University.

I further certify that the work and approach adopted is entirely original and it has not been carried out anywhere else in the same form or manner nor it has been submitted for any other degree of this or any other University.

Mr. Rajesh Kumar Pachauri has put in more than two hundred days of work in the chemical laboratory of Dayanand Vedic (P.G.) College, Orai.

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PREFACE

Present thesis deals with the preparation of mixed phthaleins (phthal-as-eins), and mixed succineins (succin-as-eins), derived from phthalic, tetra chloro phthalic, nitro phthalic and succinic anhydrides and colour of these dyes in relation to their chemical constitution.

Chapter I is introductory and contains brief historical developments of light absorption and colour in relation to chemical constitution of organic compounds in general and dyes in particular.

Chapter II contains discussion of the results obtained. The colour of these phthal-as-eins and succin-as-eins have been explained on the basis of resonance taking place between neutral and polar structures of the dye molecule containing a quinonoidal system with an effective conjugated chain. FEMO (Free Electron Molecular Orbital Treatment) produced by H. Kuhn has been applied to determine the position of the absorption band of phenol and resorcinol dyes. The chemical structures assigned to different dyes on the basis of chemical reactions and spectral studies are discussed in the later portion of chapter II.

The remaining chapter i.e. III, IV, V and VI consist of experimental part. Chapter III and IV have been divided into four sections each (i.e. 1,2,3 and 4), and chapters V and VI

have been divided into three sections each (i.e. 1,2 and 3).

The chapters III, IV and V deal with the preparation of dyes derived from α -keto acids of series A,B and C given on page(63) , respectively. Chapter VI deals with the preparation of dyes derived from β -aroyl propionic acids of series D given on page (63).

Tables giving brief account of each dye are attached in the end of the thesis.

CONTENTS

	<u>PAGE</u>
<u>CHAPTER - I</u>	
INTRODUCTION	1 - 61
<u>CHAPTER - II</u>	
RESULT AND DISCUSSION	62 - 124
<u>EXPERIMENTAL</u>	125 - 275
<u>CHAPTER - III</u>	
Section -1 : Dyes derived from O-(4-amino 3-chloro benzoyl) benzoic acid.	127 - 138
Section -2 : Dyes derived from O-(3-carbmethoxy 4-hydroxy benzoyl) benzoic acid.	139 - 147
Section -3 : Dyes derived from O-(2-hydroxy 5-methyl benzoyl) benzoic acid.	148 - 156
Section -4 : Dyes derived from O-(3,4-dimethyl benzoyl) benzoic acid.	157 - 165
<u>CHAPTER - IV</u>	
Section -1 : Dyes derived from O-(4-amino 3-chloro benzoyl) tetra chloro benzoic acid.	166 - 177
Section -2 : Dyes derived from O-(3-carbmethoxy 4-hydroxy benzoyl) tetra chloro benzoic acid.	178 - 186
Section -3 : Dyes derived from O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid.	187 - 194
Section -4 : Dyes derived from O-(3,4-dimethyl benzoyl) tetra chloro benzoic acid.	195 - 202

CHAPTER - V

Section -1 : Dyes derived from O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid.	203 - 213
Section -2 : Dyes derived from O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid.	214 - 222
Section -3 : Dyes derived from O-(3,4-dimethyl benzoyl) m-nitro benzoic acid.	223 - 231

CHAPTER - VI

Section -1 : Dyes derived from β -(4-amino 3-chloro benzoyl) propionic acid.	232 - 242
Section -2 : Dyes derived from β -(2-hydroxy 5-methyl benzoyl) propionic acid.	243 - 251
Section -3 : Dyes derived from β -(3,4-dimethyl benzoyl) propionic acid.	252 - 259
TABLES (BRIEF ACCOUNT OF EACH DYE)	262 - 275

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INTRODUCTION

PART-A

Colour plays a peculiar dominant role in our life, and yet for the most part it is a role that goes largely unappreciated. Most members of the human race have the ability to perceive colours, and since the dawn of civilization man has attempted to reproduce the colours of nature, for both aesthetic and purely functional purposes. The exploitation of colour has never been as evident as it is today, and vast industries are now directly or indirectly dependent on the availability of artificial colorants. Colour making and colour using industries contribute greatly to the economy of any industrialised country. Because of the commercial importance of colouring matters, considerable interest has been shown in the theoretical and empirical evaluation of relationship between colour and molecular structure. This interest has been accentuated by the widening areas into which colour and colorants now intrude, and colour structure relationship are now a value to scientists working in many seemingly unrelated disciplines.

A brief examination of ones surroundings will soon convince him of how intimately colorants invade our environment. Painted walls, clothing, carpets, plastic veneers, food all contain these substances. Even so called white objects, such as this page, are normally rendered whiter than white by the

incorporation of special dyes, known as fluorescent brightening agents. Thus dyes and pigments become more than pretty chemical curiosities to the analytical chemists and forensic scientists, and also to the physicians in diagnostic medicine, and to the biologist involved in histological studies. Business and industry save apart, dyes and pigments enjoy their applications in science¹, biology², medicine³⁻³⁰, engineering, architecture and technology³¹⁻³³, art and philosophy, psychology³⁴, and above all in modern living³³. Liquid crystal systems, high energy radiation sensors and organic dye lasers³⁵⁻³⁹ are further recent examples of the varied uses to which synthetic colouring matters can be put. It is perhaps than not surprising that the Organic chemists has been called upon to provide colorants for a bewildering range of applications, and this demand currently continues unchecked.

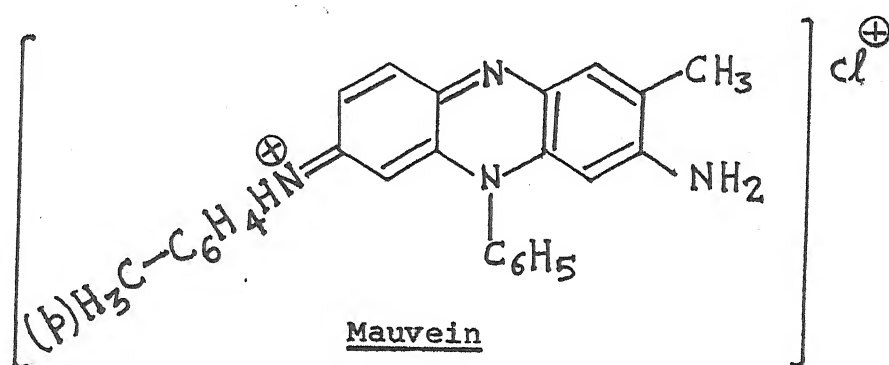
NATURAL COLORANTS :

In anciant times, the materials used to produce colours were a few in number and were obtained from vegetable or animal sources. Three of the most prized colours were: the blue of Indigo which Egyptians have been using as early as 3000 B.C., the red of Medder, known as Turkey red or Alizarim and then yellow of Saffron, obtained from 'Carthamus tinctorious'. Other colouring matters were those of animal origin. 'Tyrian purple', obtained from a small snail 'Murex bandaris' and 'Cochineal' obtained from dried bodies of female insect, 'Caecus cacti'.

SYNTHETIC COLORANTS :

The modern synthetic dye-stuffs industry, which now utilizes multibillion dollar capital, owed its creation to the academic research of Perkin⁴⁰ and the vigorous progress of its early years is the efforts of such leading organic chemists like Hofmann, Baeyer, Caro, Griess, Graebe, Liebermann, Otto Fischer, Emil Fischer, Witt, Nietzki⁴¹ and others. Subsequently, the development of organic dyes passed largely into the hands of research chemists, more actively concerned with the industry, such as Sandmeyer, Heumann, Schmidt, Green⁴² etc.

As early as 1843, Hofmann had observed that aniline as prepared at the time gave red colour under certain conditions. In 1856 Perkin⁴³ oxidized aniline sulphate with potassium dichromate and obtained a purple dye called MAUVE.



Mauvein or Aniline purple, which became the first coaltar dye to be manufactured commercially, and was the sensation of the 1862 World Exhibition in London. The first coaltar dye

cought on and the race for new dyes and colours began. From a waste product coal tar was transformed into a commodity of usefulness. Synthesis of Martius yellow, Caro's Induline Blue and Hofmann's violet followed quickly and accepted widely. The discovery that colouring matters could be prepared by oxidation of aniline led to the study of the behaviour of this base towards various other oxidizing agents. Soon thereafter the bright red dye FUCHSIN was prepared in 1859 by Verguin in Lyons, France, by oxidation of aniline by tin chloride, which made even greater impact than MAUVE. After Hofmann showed that FUCHSIN is a derivative of the TRIPHENYL METHANE, this class of dyes was investigated extensively and came into widespread use.

The discovery of the early synthetic aniline dyes was necessarily the result of intuitive following of clues derived from fortuitous experiments, since the constitution of even benzene was unknown. In 1865, Kekule published his theory of the structure of benzene, and thus paved the way for elucidation of structure of organic compounds aromatic in nature and for the development of the dye industry on a rational basis. The artificial dyes, although more brilliant, were less permanent than the natural dyes. Chemists set to work analyzing the structure of the natural products⁴⁴⁻⁴⁸. The structure of alizarin, the popular red dye from root of madder, was quickly determined in 1868 by Carl Graebe and Carl Liebermann⁴⁹ to be a derivative of Anthracene. Benzene, naphthalene and anthracene are colourless

products of coal tar distillation. By simple chemical addition of chromophoric groups⁵⁰, beautiful dyes can be created. This finding in the nineteenth century excited the fashion world to colourful fantasies. Graebe and Liebermann in 1868 afforded synthesis of alizarin⁵¹. In 1869 Graebe, Liebermann and Perkin achieved its commercial production. This followed the production of a family of alizarin like dyes with different colours. In 1871 FLUORESCEIN was prepared by Baeyer and in the same year CARO prepared Eosine after the commercial production of resorcinol. Whilst attention of chemist was directed towards the synthesis of alizarine, another class of dye stuffs - the azodyestuffs - appeared in commerce in 1876. Griess had already synthesised azo compounds in 1862, and one member of group BISMARCK BROWN had already been prepared on commercial scale since 1863. In 1875, Caro discovered CHRYSOIDINE, indicated the technical value of the Griess method of preparing azo compounds, when azo-dyestuffs were first introduced, it was considered that only orange and yellow colours could be obtained in this series. This idea was dispelled by discovery of FAST RED-A by Caro in 1878; thus Heinrich Caro⁵² contributed much to the synthetic dye industry.

Since then the progress in the field of dyes has been very rapid⁵³⁻⁸¹. To list a few milestones in the progress - Direct dyes from azo compounds for cotton were introduced in 1880; Sulphur colours from coal tar derivatives in 1893; Anthraquinone dye, Vat dyes, in 1901; Azoic dyes or Ice colours in 1911;

Acetoacetanilides in 1923; Phthalocyanines in 1934; Fluorescent Brightening agents in 1940 and Fibre Reactive Procion dyes in 1956. Thus natural dyestuffs were almost completely displaced by synthetic colorants. Fundamental research on new dyes is constantly in progress⁸²⁻⁹⁶ and thus synthetic dyes are dominating the field now. Today the industry occupies an important place among the major chemical industries.

PIGMENTS :

Dyes for solvents, oils, waxes or plastics are either soluble in these media, els, so finely divided that they may be effectively dispersed through out to give high colour strength. These insoluble colouring substances are called PIGMENTS⁹⁷.

CLASSIFICATION :

The synthetic dyes have been classified in various ways, but the following two are important one.

1. ON THE BASIS OF METHODS OF APPLICATION :-

On the basis of methods of application dyes have been classified into following types:-

- | | |
|---|--------------------|
| (i) Acid dyes | (ii) Basic dyes |
| (iii) Direct dyes | (iv) Mordant dyes |
| (v) Ingrain dyes | (vi) Disperse dyes |
| (vii) Vat dyes(indigo and anthraquinone dyes) | |

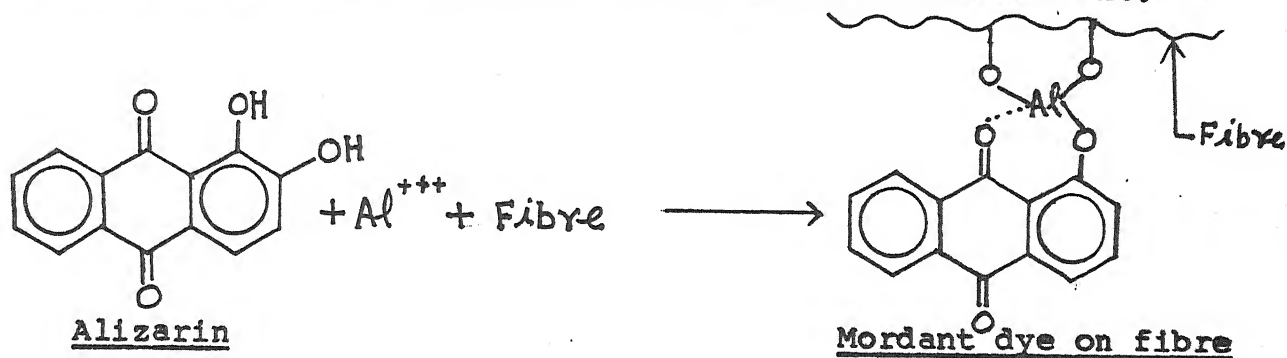
- (viii) Sulphur dyes (ix) Synthetic fibre dyes
 (x) Other synthetic dyes.

(i) Direct Dyes :

These contain acidic or basic groups and combine with polar groups in the fibre, such dyes colour a fabric directly when the fibre is immersed in a hot aqueous solution of the dye. Direct dyes are used to dye wool and silk. The two examples are, Naphthol yellow and Martius yellow.

(ii) Mordant Dyes :

The class of dyes require a pretreatment of the fibre with a mordant material designed to bind the dye. The mordant becomes attached to the fibre and then combines with the dye to form an insoluble coloured complex. This complex is called a lake. Commonly used mordants are the oxides of aluminium, iron and chromium. Alizarin is an example of a mordant dye. It gives different colours when used with different mordants. It gives a red colour with aluminium and tin salts, brownish red tones with a chromium mordant, and black violet with an iron mordant.

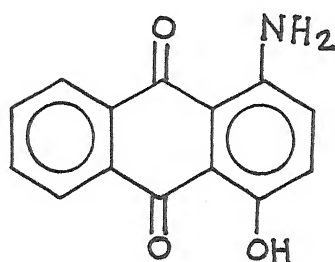


(iii) Ingrain Dyes :

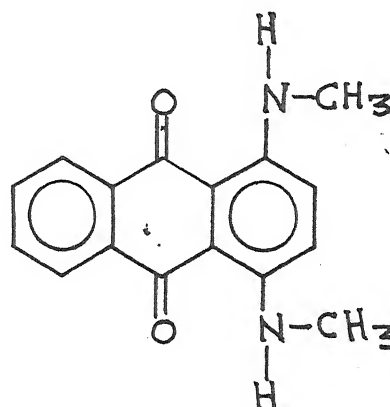
The azo dyes are good example of ingrain dyes. The cloth to be dyed is first soaked in an example solution of a phenol (usually Naphthol) and dried. It is then immersed in a cold alkaline solution of a diazonium salt.

(iv) Disperse Dyes :

These dyes are involuble in water, but are capable of dissolving certain synthetic fibres. Disperse dyes are usually applied in the form of a dispersion of finely divided dye in a soap solution in the presence of some solubilizing agent such as phenol, cresol, or benzoic acid. Celliton fast pink B (1-amino, 4-hydroxy anthraquinone) and Celliton fast blue B (1,4-N, N'-dimethyl amino anthraquinone) are examples of disperse dyes.



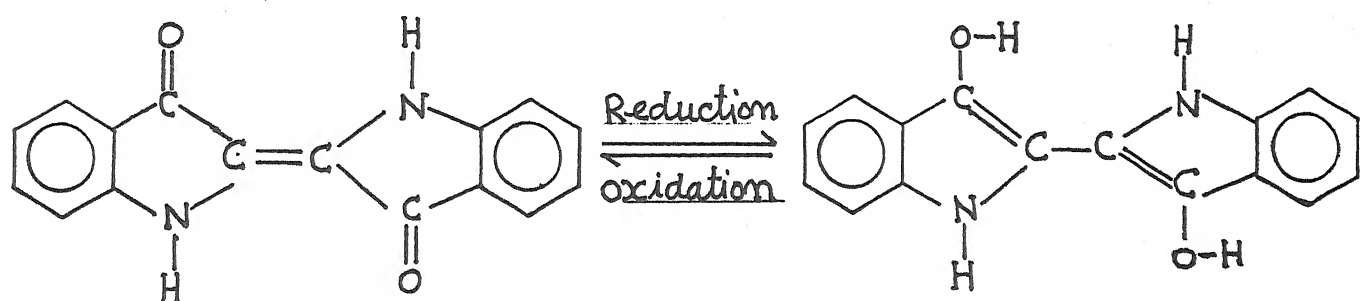
Celliton fast pink-B
(1-amino, 4-hydroxy
anthraquinone)



Celliton fast blue-B
(1,4-N, N' dimethyl
anthraquinone)

(v) Vat Dyes :

These dyes are involuble in water, but on reduction with sodium hydrosulphite yield alkali soluble forms (Leuco-compounds) which may be colourless. It is in this form they are introduced into the fabric. The reducing operation was formerly carried out in wooden vats, giving rise to the name 'VAT DYES'. After the reduced dye has been absorbed in the fibre. The original insoluble coloured dye is reformed by oxidation with air or chemicals. Indigo is the best vat dye.

Indigo blue

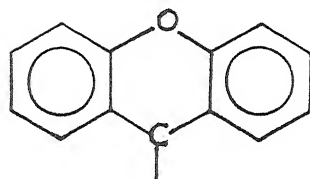
(Blue; water involuble)

Indigo white(Colourless; water soluble-
A Leuco-compound)2. ON THE BASIS OF CHEMICAL COMPOSITION & STRUCTURE :-

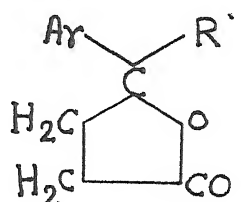
Chemical dyes have been classified into a number of classes. This classification is mainly useful for the chemists, who are mainly interested in the chemical constitution of the dyes.

- | | |
|---|-------------------------------|
| (i) Nitroso dyes | (ii) Azo dyes |
| (iii) Nitro dyes | (iv) Diphenyl methane dyes |
| (v) Triphenyl methane dyes | (vi) Heterocyclic or Azine dy |
| (vii) Phthalocyanine dyes | -s |
| (viii) Vat dyes : a. Indigo dyes b. Anthraquinone dyes | |
| (ix) Sulphur dyes : a. Thiazine dyes b. Thiazoles | |
| c. Sulphur blacks. | |
| (x) Xanthen dyes : a. Fluoranes b. Phthaleins | |
| c. Pyronines d. Succineins | |
| e. Rosamines & f. Rhodamines. | |

The present thesis deals with phthaleins which are quite related to xanthen dyes having a common structural feature as shown in (a), and succineins having a structural feature as shown in (b). These dyes are prepared by condensing various phenols, aromatic aminophenol with phthalic anhydride or substituted phthalic anhydride and succinic anhydride respectively in the presence of a dehydrating agent (anhydrous zinc chloride, conc. sulphuric acid).

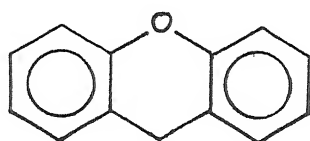


(a)

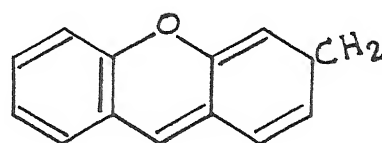


(b)

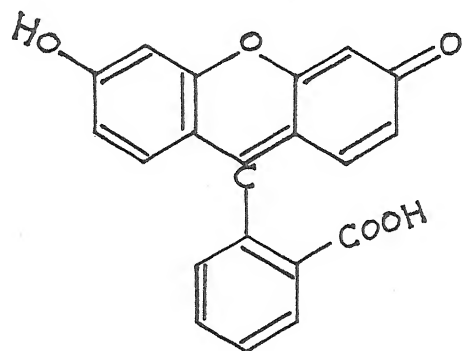
Xanthen (A) dyes are characterised by the presence of dibenzopyran nucleus (C,D). They have been classified in various way; with special names for groups and sub-groups. Most conveniently these have been divided into three general groups; an acid group characterised by hydroxyl substituents for e.g. fluorescein (C), a basic group characterised by amino substituents e.g. rhodamines (D), and a mixed type characterised by both an amino and hydroxyl substituents, the rhodols.



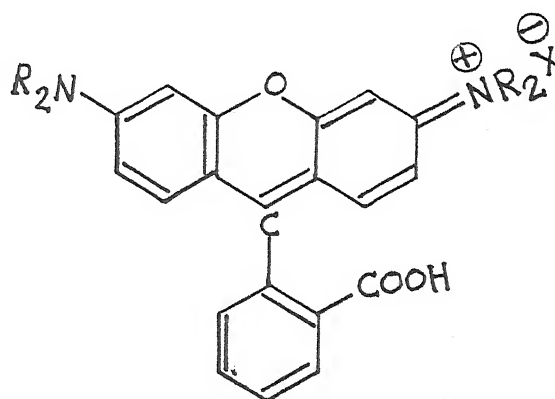
XANTHEN (A)



3H-Iso Xanthen (B)



Fluorescein (C)
(Quinonoid form)

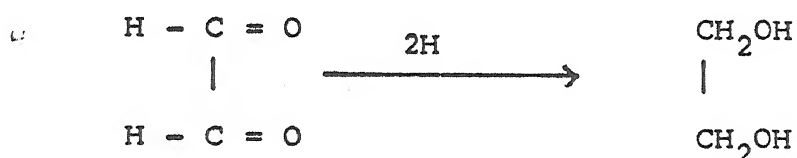
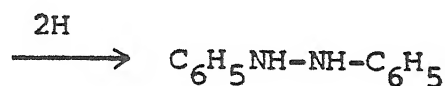
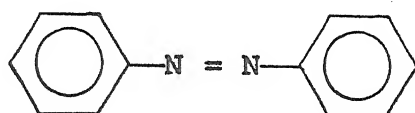


Rhodamines (D)

PART - BRELATIONSHIP BETWEEN COLOUR AND CHEMICAL CONSTITUTION OF THE MOLECULES

Graebe and Liebermann⁴⁹ in 1868 pointed out that unsaturation was important for producing colour and that reduction of coloured compounds always resulted in the formation of colourless products for e.g.

- (i) Glyoxal is coloured but its reduced product is colourless.
 (ii) Azobenzene is coloured but its reduced product 'hydrazo-benzene' is colourless.

Glyoxal(Coloured)Ethyleneglycol(Colourless)Azobenzene(Coloured)Hydrazo benzene(Colourless)

These unsaturated colour bearing groups are called as chromophores and the substance containing chromophoric groups are known as CHROMOGENES. Besides these unsaturated chromophoric groups the other groups by its presence in the molecule caused an intensification of colour. These groups were called Auxochromes.

The important auxochromes are hydroxyl and amino groups. These groups did not in themselves produce colour. The auxochromes could produce either a hypsochromic effect i.e. a shift in the absorption band to shorter wavelength or a bathochromic effect i.e. shift in the absorption band to longer wavelength. O.N. Witt⁴⁵ (1876) in his 'Chromophore-auxochrome theory' brought fourth the importance of unsaturation in the appearance of colour. Later on Neitzki⁹⁸, Armstrong⁹⁹ etc, gave their theories regarding colour and chemical constitution. All these theories, rules and suggestions interpreted colour in the term of structure without much regard to its physical cause. Later on it became quite evident that although these theories, rules and suggestions were very helpful as guide in the production of dyes but have very limited validity and on the basis of these no general relationship between colour and chemical constitution could be evolved.

A complete and satisfactory explanation of colour of organic compounds was found to be associated with the absorption and transmission of light and in general with the spectrum of the molecule. The absorption of light was recognised to be associated with certain process of molecular energy changes and the processes could also take place with many other substances, besides those appeared coloured to the human eye. The colour as it appears to the human eye, is only a special case of the general features of the phenomanon of absorption of electromegnetic waves and the

colour of a substance for which human eye is sensitive, is determined by the selected absorption of the light consisting of those waves the phenomenon of absorption of light is not limited to visible part of the spectrum only but takes place in the ultraviolet and infra red portions as well.

Since white light imparts different colours to different chemical compounds, it is obvious that colour is a function of the chemical constitution of molecules.

ABSORPTION OF LIGHT BY MOLECULES :

The wave particle duality of matter when applied to electromagnetic radiation and to atomic particles, from the basis of the quantum theory which gives the de-Broglie relationship.

$$p = h/\lambda \quad \text{-- (a)}$$

where p is the momentum of the particle, λ is its wavelength and h is the Planck's constant.

The absorption and emission of light by matter¹⁰⁰ is explained by the wave property of light. An electromagnetic wave is characterised by an electric vector E , and a magnetic vector M , which form a mutually perpendicular set of axes with the propagation vector C . If the light is monochromatic of frequency ν , then the amplitudes of the electric and magnetic vectors vary periodically according to the expressions.

$$E(x,t) = E_0 \sin 2\pi \nu (x-ct + \phi) \quad \text{-- (b)}$$

$$M(x,t) = M_0 \cos 2\pi \nu (x-ct + \phi) \quad \text{-- (c)}$$

where x is the coordinate in the directions of the light propagation, t is the time and ϕ is a phase vector. The absorption of light arises mainly through the interaction of the electric vector of the light with the electrons and nuclei in the molecule. The magnetic vector is only important for an understanding of the phenomenon of optical rotation. A molecule which is initially in a state ψ_K can absorb light of frequency ν , providing there is a state ψ_n which has energy greater than ψ_K by an amount.

$$E = E_n - E_K = h\nu = hc/\lambda \quad \text{-- (d)}$$

and it is said that molecule has absorbed a photon of energy $h\nu$ and is in excited state ψ_n . The stability of the excited state is limited, and after a very short time e.g. less than 10^{-8} Sec, the excited molecule dissipates its excitation energy and comes back to the ground state ψ_K .

A molecule can exist in many excited states corresponding to its changes in rotational, Vibrational and electronic energies, all of which are quantised. Therefore, the absorption spectra¹⁰¹ can be further classified into three types.

(i) Pure rotational spectrum which is associated with changes in the rotational state of the molecules, without

simultaneous changes in the vibrational and electronic states. Since the separation in energy between the various rotational levels are relatively small, it follows from equation (d) that the corresponding frequencies are relatively low. The pure rotational spectra of all substances, therefore, occur in far infrared and microwave regions.

(ii) Rotation-vibration spectrum is associated with transitions in which the vibrational and rotational states of the molecule are altered, but in which the electronic states remain unchanged. The energy differences are greater here than in the pure rotational spectrum and, accordingly, the absorption occurs at shorter wavelengths, viz in the near infrared region.

(iii) Electronic spectrum which arises from transitions between electronic states, usually accompanied by simultaneous change in both the vibrational and rotational levels. Therefore, a broad absorption band instead of a sharp line is observed. Relatively large differences are involved in the electronic spectra, which occur at shorter wavelengths i.e. in the ultraviolet and visible region.

Since the electrons can only be raised to certain energy levels (i.e. an electron must occupy some definite orbital), ΔE must have definite value i.e. absorption of light by a molecule is not indiscriminate (continuous) but selective and this gives rise to colour. A part from the

frequency of the absorption band, colour also depends on the intensity of the absorption which itself depends on the probability of transition between the two energy levels concerned. The probability of the photon being absorbed depends on the magnitude of the transition dipole moment between the two states.

Light absorption by a molecule¹⁰² can only occur when the dipolemoment changes in that molecule. The more symmetrical the molecule, the smaller is the possibility of a transition dipole, and, therefore, the less likelihood of the absorption of light by the molecule. Calculations have shown that the greater the transition dipole, greater is the intensity of absorption.

The introduction of a group into a molecule which decreases symmetry will thus increase the transition dipole and consequently increases the intensity of absorption. At the same time, however, new 'resonance paths' may be introduced, and hence not only a change in intensity of absorption occurs due to an increase in transition dipole, but there is also a shift of the band to longer wavelengths.

ELECTRONIC ABSORPTION SPECTRA AND COLOUR OF DYES :

To understand the colour of a compound it is necessary to have a knowledge of the electronic structure of the molecule and its effect on the absorption of the light in the visible and

near ultraviolet region of the spectrum. For this purpose three main theoretical approaches to the problem have been made which are-

- (i) The Valence bond (VB) or Resonance Theory.
- (ii) The LCAO (Linear Combination of Atomic Orbitals) or molecular orbital theory.
- (iii) Free Electron Molecular Orbital (FEMO) theory.

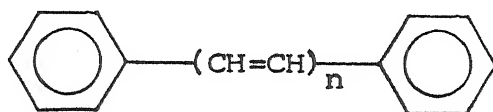
In the following account the first two methods are briefly described, while the third method is considered in some detail in connection with the phenomenon of light absorption. The FEMO approach is the most recent, the least known, and in many respects the simplest of the three.

THE VALENCE BOND OR RESONANCE THEORY :

The early studies of light absorption, it was observed that certain molecules absorbing in the visible region could be represented by two equivalent resonating structures, between which an oscillation of bonding was believed to occur. Burry¹⁰³ was the first to suggest that the colour was actually due to such oscillations, but due to rapid development of quantum theory, this observation was modified by various investigators. Lewis and Calvin¹⁰⁴, Pauling¹⁰⁵⁻¹⁰⁶, Forster¹⁰⁷ and Knott¹⁰⁸ have proposed that the colour of dyes is associated with the resonance between two or more structures which differ by displacement of an electron charge from atom to atom of the dye molecule.

Lewis and Calvin¹⁰⁴ have been able to show that colour also depends on the number of electrons involved in oscillation. Larger the number of electrons involved in oscillation deeper will be the colour.

It has been found that increased conjugation in a molecule shifts the absorption band towards longer wavelengths and thus it deepens colour e.g.(1).



I (Diphenyl polyene¹⁰²)

n	0	1	2	3	4	5	6	7
λ -max	2515	3190	3520	3770	4040	4240	4450	4650

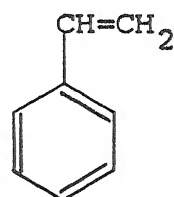
From the following equation :

$$E = E_n - E_k = h\nu = hc/\lambda \quad \text{-- (d)}$$

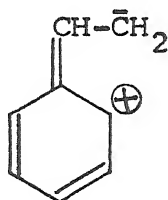
It is evident that factors responsible in decreasing of ΔE will shift the band to longer wavelengths. Resonance among the charged structures lowers the energies of both ground and excited states, and since charged structures contribute more to the excited than to the ground state, the lowering of energy

will be more prominent in the former than in the latter. Thus a greater resonance among the various charged forms results in a deepening of colour.

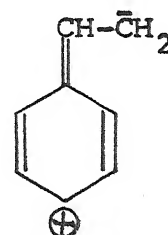
From the above going discussion it can be inferred that a given chromophore will not necessarily give absorption bands in the same position of the spectrum, the rest of the molecule also affects it. Benzene has a definite ultraviolet absorption spectrum (255 nm), ethylene has a ultraviolet spectrum (185 nm), allyl benzene has a spectrum (249 nm) which is equivalent to the superimposition of all these spectra of benzene and ethylene. However, styrene has a quite different spectrum (282 nm) where the fine structure of benzene is absent. Therefore, it can be observed that in styrene, the benzene nucleus is not in the same state as it is present in benzene itself or allyl benzene. This observation can be explained by assuming styrene to be a resonance hybrid of the following structures:



(II)



(III)



(IV)

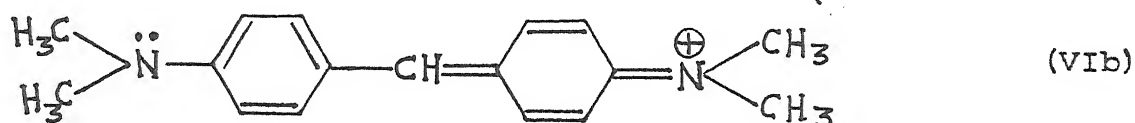
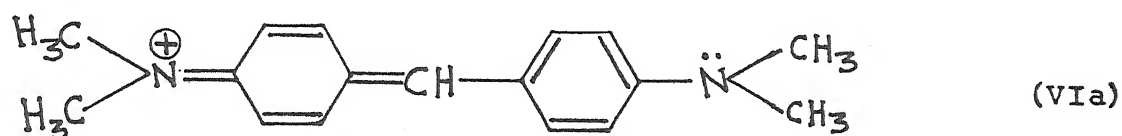
The cyanine dyes studied by Brooker and his Coworkers¹⁰⁹, are intensively coloured substances exhibiting a high degree of resonance. These dyes can be represented by the general structure

(Va and Vb) .



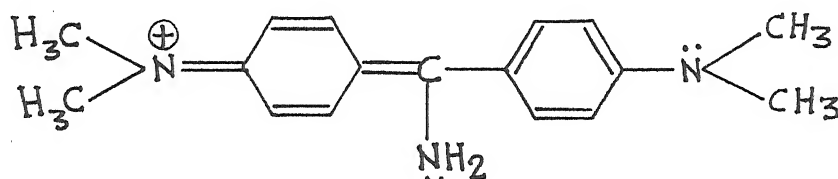
If aromatic ring systems are made part of the conjugated chain of a cyanine, the characteristic properties of the chromogene are not altered. Thus the system will still be isoconjugate with an odd alternant hydrocarbon anion, and will absorb at long wavelengths by virtue of the presence of a non bonding molecular orbital. The di and Tri-aryl methane dyes are the example of this type.

Thus for e.g. Michler's Hydrol Blue (a diaryl methane dye) which is resonance hybrid of two equivalent structures (VIa and VIb), absorbs at 607.5 nm in 98% Acetic acid.



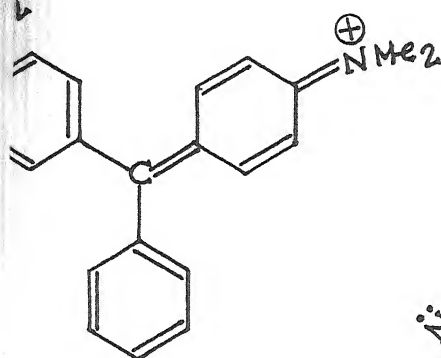
The Auramine (VII), an important commercial dye of diaryl methane series, which is formed by the attachment of

an amino group to the Central carbon atom of Michler's Hydrol Blue, shows large hypsochromic shift that results from the strongly electron donating amino group. It absorbs at 434 nm in ethanol. Substituents other than amino exert a hypsochromic shift related to electron donating ability, for e.g. attachment of the weaker ethoxy group to the central atom of Michler's Hydrol blue given a smaller shift, and the dye is purple (λ -max calc. 525 nm).



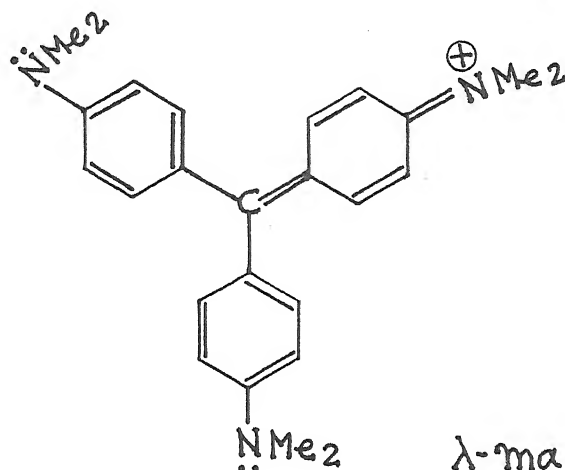
(VII)

The triaryl methane dyes, on the other hand, can be divided into two distinct types, those with two terminal amino groups e.g. Malachite green (VIII) and those with three terminal amino groups, e.g. crystal violet (IX). From the foregoing description it would be expected that resonance among an increasingly larger number of resonating structure would deepen the colour. But the case of Malachite green (VIII) and crystal violet (IX), proves contrary to the expectation as the colour of former is deeper than the latter. Malachite green has two resonating forms where as crystal violet has three resonating forms.



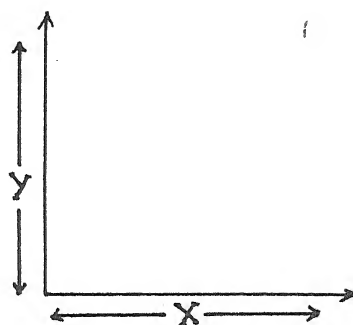
λ -max 621 nm
(in acetic acid)

(VIII)



(IX)

λ -max 589 nm



Malachite green shows two absorption bands, one at longer wavelengths (λ -max 621nm 98% acetic acid) as expected for the attachment of neutral conjugating group at any position in the chromogene, and a second band at shorter wavelengths (λ -max 427.5nm) and as this provides a yellow component to the colour, the dye is green rather than blue. Polarisation studies have shown that the two transitions are polarised along mutually perpendicular axes¹¹⁰. The longer wavelength band is due to Polarisation along x-axis, and the shorter wavelength band along the y-axis.

Let us consider the hypsochromic effect shown by substituting dimethyl amino group in Malachite green to get

crystal violet. According to resonance theory the crystal violet ion possesses a high symmetry, consequently a number of level will have the same energy value (degeneracy) although the total number of levels has actually increased and this is responsible for the remarkable hypsochromic effect. The average separation of oscillating charge is, however, increased so that the absorption band is displaced towards shorter wavelengths while the intensity has increased due to the increase in the absorption probability proportionately with the increase in the number of corresponding levels. Lewis and Calvin¹⁰⁴ proposed that the oscillation of a charge along one direction only (say horizontal) is responsible for the production of colour. In Malachite green all the positive charge is involved in the linear oscillation (horizontally) while in crystal violet the positive charge can oscillate horizontally as well as vertically. Thus $2/3$ of the positive charge is effectively oscillating horizontally in crystal violet. Hence Malachite green has deeper colour than crystal violet.

MOLECULAR ORBITAL (MO) THEORY :

According to the theory of molecular orbitals(MO)¹¹¹⁻¹¹³ the absorption of ultra violet and visible light corresponds to the disturbance of the electron cloud of a molecule, resulting in the formation of an electronically excited state. According to quantum theory, a molecule can exist only in a limited number of discrete energy states. The electronic structure of a molecule

can then be built up by feeding the electrons one after another in the lowest available quantum states in accordance to the Aufbau-Principle. A concept of united atoms i.e. an atom whose atomic number is equal to the sum of those of the two separated atoms is helpful to understand the filling of electrons in the M.O. The electrons which in the united atom occupy an excited level are the 'loosening' or antibonding electrons and those which do not are the 'bonding' ones. Electrons in the atoms which remain unaffected by the process of molecule formation are said to be 'non-bonding' electrons.

It is possible to consider the phenomenon of light absorption from the point of view of M.O. A molecule is excited when one electron is transferred from an Orbital of lower to one of the higher energy. Such transitions can occur only between 'Permitted' orbitals. In molecules a g state must go to U state, or Viceversa; transitions U-U* and g-g* are forbidden (U stands for antibonding molecular orbital and g for bonding molecular orbital).

The ethylene molecule in its ground state has, in addition to σ bond, a π g orbital (bonding orbital), and in the first excited state a π u orbital (antibonding orbital) in which one electron has been excited. For the transfer of one electron from a π g to a π u orbital, a large amount of energy is required and the molecule absorbs in the ultra-violet region.

In compounds containing two or more double bonds in conjugation delocalisation of bonds takes place and the molecular orbital formed covers all the carbon atoms of the system. The electron, therefore, has greater freedom of movement than in localised bonds and the total energy of the system is lowered which decreases the energy difference (ΔE) between the highest occupied and lowest unoccupied π -orbitals. Thus as the conjugation extends, the absorption of light takes place at longer wavelengths.

Benzene molecule is symmetrical with all the carbon atoms having equal charges of unity and hence there is no transition dipole in the benzene molecule. It is not expected to absorb light and hence it is colourless. However, a weak absorption in the ultra violet region is exhibited. Nitrobenzene is not symmetrical and has unequally charged carbon atoms. Unequal charge produces a definite dipole moment in the compound, which is responsible for the high transition dipole, and consequently absorption of light may be expected at longer wavelength, further more since nitrobenzene has an extended system of conjugation, the energy difference between the highest occupied and the lowest unoccupied orbital is decreased, and so that it absorbs at longer wavelengths than that of benzene. Nitro aniline (orange red) having more extended conjugation and greater separation of charge, absorbs light at longer wavelengths than Nitrobenzene and Aniline. Thus in

general any group which conjugates with benzene ring shift the frequency of the absorbed light to lower region.

The valence bond approach to colour is only satisfactory qualitatively, but the M.O. method appears to be more promising from a quantitative point of view. It has been possible to calculate the light absorption of many molecules with its application, and a good agreement has been obtained¹¹⁴ between calculated and observed values.

FREE ELECTRON MOLECULAR ORBITAL (FEMO) THEORY :

It has already been shown in foregoing discussion that all dyes of practical interest have a complicated constitution and the colour is strongly influenced by even a slight structural changes. Hence the problem of predicting the colour of Organic dyes from quantum mechanical consideration is necessarily an intricate one. To avoid a rigorous mathematical treatment in solving this problem, it is essential to consider a highly simplified quantum mechanical model, which was originally proposed by Sommerfield¹¹⁵ to describe the metallic state. These ideas were later on extended to, Organic molecules by Bayliss¹¹⁶, Simpson¹¹⁷, Kuhn¹¹⁸⁻¹¹⁹ and Platt¹²⁰ which formed the basis of the method known as the FEMO method. This method has been successfully applied to spectroscopic problems.

The free electron method is the simplest of the molecular orbital method for conjugated molecules, and in certain

cases can be remarkably successful in the calculation of transition energies. Similar to valence bond and molecular orbital treatments, in FEMO treatment too, all the carbon and hydrogen atoms are presumed to lie in one plane, so that various atomic orbitals are of either sigma or Pi types. The fundamental approximation in this approach is the sigma Pi separation principle, i.e. the assumption that the sigma and Pi-electrons can be treated independently. Consequently this assumption specifically a characteristic feature that the electrons in conjugated Polyenes behave as if they were in one dimensional box, which means that their potential energy is set equal to zero at all points inside this box. The length of this box is supposed to be approximately the same as that of the conjugated system.

According to wave theory of matter the motion of electron backwards and forwards across the molecule can be described by a wave, whose wavelength λ is given by the well-known de Broglie relationship (1) where h is Plank's constant, m the mass of the electron and v the velocity of the electron.

$$\lambda = h/mv \quad \text{----- (1)}$$

Permanent motion of electron is only possible if the associated wave motion does not set up destructive self interference. Expressing this limitation on the wave motion in mathematical form.

$$L = n \cdot \lambda/2 \quad \text{----- (2)}$$

where L is the length of the potential well and n , is the quantum number of the energy level which is restricted to the integral values $1, 2, 3, 4, 5, 6 \dots \infty$. The velocity of the electron can be evaluated from equation (1) and (2), whence

$$V = n \cdot h / 2m \cdot L \quad \text{----- (3)}$$

The energy of the electron will be sum of its Kinetic energy ($\frac{1}{2}mv^2$) and its Potential energy (arbitrarily zero) and this will correspond to the energy of the molecular orbital in which the electron resides, i.e.

$$E_n = \frac{1}{2}mv^2 = \frac{n^2 h^2}{8m \cdot L^2} \quad \text{----- (4)}$$

Equation (4) indicates that the electron can be confined to a series of molecular orbitals, depending on the magnitude of the integer n , a quantum number. The energy of the orbitals, E_n , increases with n , as does the number of nodes in the molecular orbital wave function. No limitation is placed on the number of possible orbitals.

The π electron structure of 1,3 butadiene is then obtained by assigning two electrons of opposite spin to the lowest orbital ($n=1$) and two similarly spin paired electrons to the second orbital ($n=2$). The absorption of light is then assumed to involve promotion of one of these four electrons to any of the higher energy vacant orbitals. Equation (4) can then be used to calculate transition energies. The only uncertain

parameter in this equation is L , the length of the potential well. It is usual to regard the L as equal to the length of the molecule (assuming that the molecule is distorted into a straight line), plus one additional bond length at each end of the molecule for e.g. 1,3 butadiene has an average bond length of 1.4\AA , which gives a value of 7\AA for L .

Using equation (4), the transition energy for the promotion of an electron from an orbital n to orbital $n+1$ will be given by

$$E_n \longrightarrow n+1 = \frac{h^2}{8m \cdot L^2} (2n+1)^2 \quad \text{----- (5)}$$

To evaluate the transition energy of the first absorption band, the value of n for the highest filled orbital must be found. A neutral Polyene with N atoms will have N -electrons, and thus $N/2$ molecular orbitals will be occupied, i.e. the quantum number for the highest filled orbital will be equal to the number of atoms divided by 2. Thus the transition energy is given by:

$$\Delta E_1 = \frac{h^2}{8m \cdot L^2} (N/2+1)^2 - (N/2)^2 = \frac{h^2}{8m \cdot L^2} (N+1) \quad \text{-----(6)}$$

This expression can be modified further by recognising that $L = (n+1)d$, where d is the inter nuclear bond length (assumed uniform):

$$E_1 = h^2 / 8m \cdot d^2 = 1/(n+1) \quad \text{----- (7)}$$

For 1,3 butadiene, 6 or 7 give a first transition energy of

about $3 \times 10^4 \text{ cm}^{-1}$, or a wavelength of 325 nm. The experimental value of 220 nm may seem inductive of poor agreement, but in view of the many gross approximations inherent in the FEMO method, and its great simplicity of approach, the agreement is remarkably good.

When an electron is supposed to stay inside a rectangular box the standing waves are obtained only under certain conditions and the Kinetic energy, $E = m/2(v_x^2 + v_y^2 + v_z^2)$, where v_x , v_y and v_z are the respective components of the velocity of the electron parallel to the three edges of the rectangular box, is restricted to the discrete values represented by the following expression:

$$E_n = m/2 \left(\frac{h n_x}{2A m} \right)^2 + \left(\frac{h n_y}{2B m} \right)^2 + \left(\frac{h n_z}{2C m} \right)^2$$

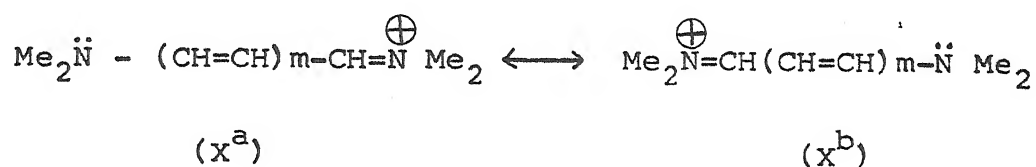
$$= \frac{h^2}{8m} \left[\frac{n_x^2}{A^2} + \frac{n_y^2}{B^2} + \frac{n_z^2}{C^2} \right] \quad \text{----- (8)}$$

It can be well noted here that a close analogy exists between the equation (4) and (8).

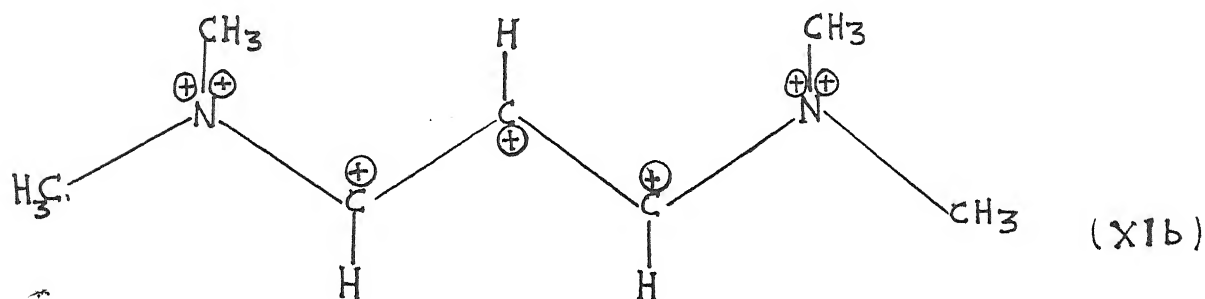
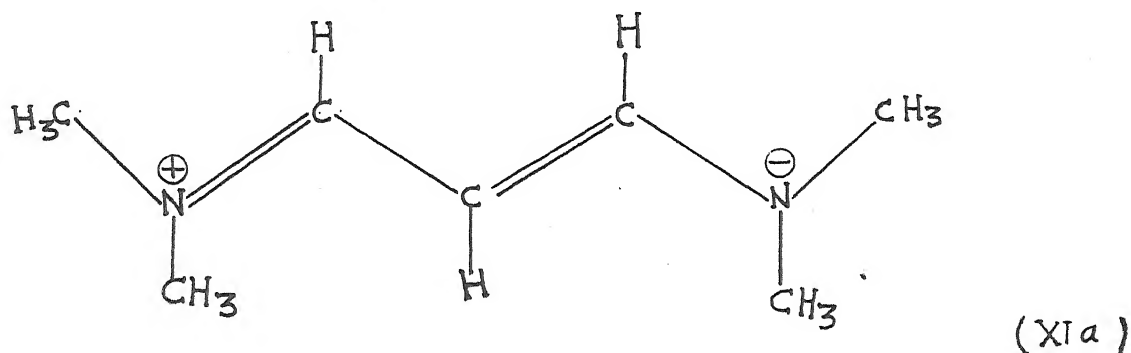
Though a satisfactory method for the direct comparison of the calculated value with that of experimental data has not been yet found, still a simple application and extension of the treatment permits a determination of the position of the absorption band of simple dye in the visible region. It can be noted that the first electronically excited state of Polyene of a simple

dye containing conjugated chain is derived from the corresponding group state by the promotion of an electron from the highest occupied level to the lowest unoccupied level.

The series of the compound known as Cyanines typified by (x), are ideally suited for the FEMO method, since they show appreciable bond uniformity, the uniformity of bond length arises from the resonance interaction $(x^a) \longleftrightarrow (x^b)$



A symmetrical cyanine dye molecule such as (XI^a) may be considered here in order to find a simple plausible explanation for its electronic absorption band in the visible region, here the C, N and H atoms are linked by σ bonds and are located in a common plane (Fig. XI^b).



Each carbon atom and each N atom uses three valence electrons to form the σ bonds in the molecule. The π electronic system in the Cyanine dye molecule is formed by the contribution of the fourth valence electron of each carbon atom and the remaining valence electrons of the two terminal N atoms. These electrons are placed in the electrostatic field of the molecular skeleton. They will be attracted by the positive charge of the C and N atoms, but their wave functions must have a node at all points of the plane of the molecule. They form an electron gas which in the shape of a charge cloud stretches along the Cyanine chain, both above and below the plane of the molecule, N has five valence electrons and in the above cyanine dye XI^a. Three are used to form σ bonds, thus N atom with no charge sign contributes two electrons to π electron gas and the N atom with the formal plus charge yields one π electron. In addition to this each carbon atom contributes one π electron, and we find a total of six π electrons or 3 π electron pairs in this case.

Now a single π electron may be considered in the electrostatic field of the rest of the molecule and it should be assumed for a moment that it can only move in the direction of the Zig-Zag line connecting C and N atoms in the chain. The potential energy of the electron is then roughly constant alongwith chain since the electron is practically in the coulomb field of the nearest C or N atom only, while the field of the more distant C and N atom is neutralised by other π -electrons.

Consequently, this electron can move almost freely along the Zig-Zag line, but not beyond the ends of the chain (leaving stretching). Thus this electron is in the same condition as a free electron considered before in one dimensional box and the length L of the Zig-Zag line corresponds to the length of the box. It must be noted, however, that the component of the motion of the π electron in the direction perpendicular to the Zig-Zag line connecting C and N atoms in the chain has been neglected here (XI^b).

In the normal state of the molecule (XI^a), the three electron pairs present in the resonating chain occupy the three lowest levels. The light absorption is caused by a transition of an electron from the highest occupied state with $n=3$ to the next state with $n=4$. Accordingly the energy difference ΔE , between these states is as given below:

$$\begin{aligned} E_4 - E_3 = \Delta E &= \frac{(4h)^2}{8mL^2} - \frac{(3h)^2}{8mL^2} \\ &= \frac{7h^2}{8mL^2} = 6.1 \times 10^{-12} \text{ erg.} \end{aligned}$$

$$\lambda_{\text{-max}} = \frac{hc}{\Delta E}, \text{ where } c \text{ is the velocity of light}$$

$$= \frac{(6.624 \times 10^{-27}) (2.998 \times 10^{10})}{6.1 \times 10^{-12}}$$

$$= 3.3 \times 10^{-5} \text{ cm}$$

$$\lambda_{\text{-max}} = 330 \text{ nm}$$

This value is in good agreement¹¹² with the experimental data viz. 313nm.

Let us consider a symmetrical cyanine dye with J. conjugated double bonds in the resonating chain connecting the two N atoms. The number of electrons in the chain is 2J+2, and the absorption band corresponds to a jump of an electron from the level J+1 to level J+2. To express the energy difference, ΔE , between these levels an equation is obtained from equation (4) (Page).

$$E = \frac{h^2}{8mL^2} (J+2)^2 - (J+1)^2 = \frac{h^2}{8mL^2} (2J+3)$$

$$\text{Thus } \lambda\text{-max} = \frac{hc}{\Delta E} = \frac{8mc}{h} \cdot \frac{L^2}{2J+3} \quad \text{----- (9)}$$

This remarkable result indicates that (in this approximation) the position of absorption band is determined by the chain length L and by the number of π electrons (2J+2), since m, h and c are universal constants; λ -max does not depend upon any specific properties of the atoms along the chain.

The length of the Zig-Zag chain which connects the C and N atoms is J x 2l, where l is bond length of chain elements; the average bond length, $l=1.39^\circ\text{A}$ has been taken for calculations on the basis of approximations considered by H. Kuhn¹¹⁰⁻¹¹⁹. The electron gas stretches by a certain length, $\propto l$, to both sides of each terminal N atom. Thus a more satisfactory value of L is

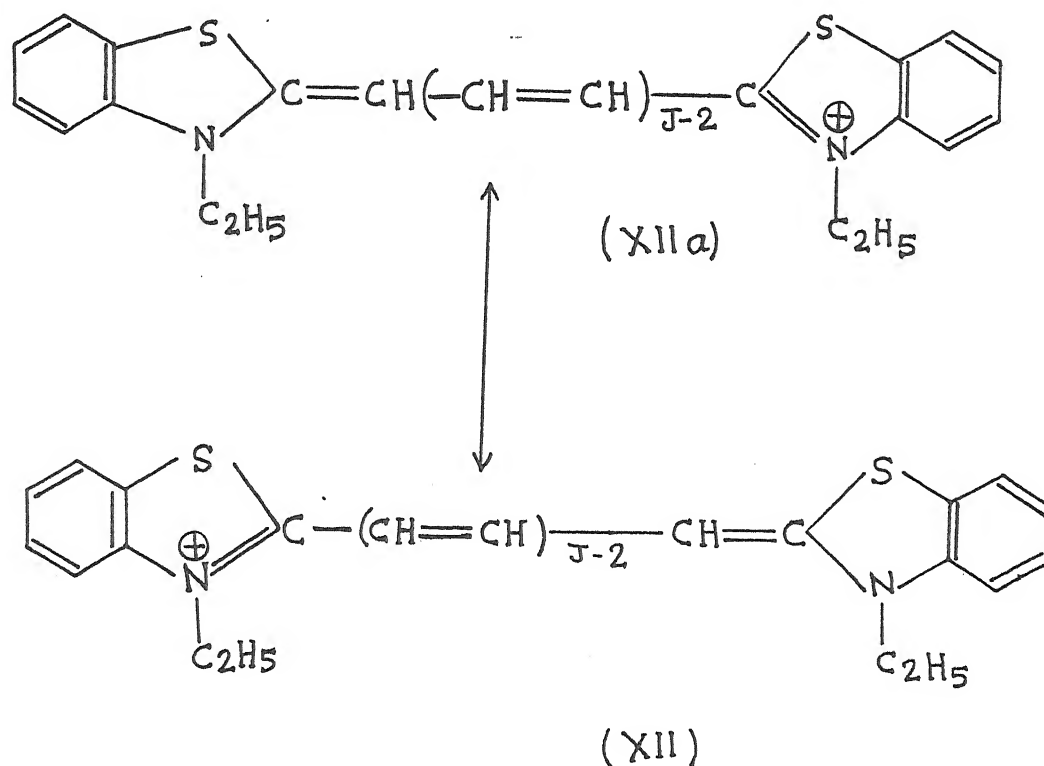
given by following expression:

$$L = J \times 21 + 2 \quad 1 = 21 (J + \alpha)$$

Now according to equation (9),

$$\begin{aligned} \lambda_{\text{-max}} &= \frac{8mc}{h} \cdot \frac{41^2 (J + \alpha)^2}{2J+3} \\ &= 127 \frac{(J + \alpha)^2}{(J+3/2)} \text{ (in nm)} \quad \text{----- (10)} \end{aligned}$$

In conjugated Polyenes, symmetrical cyanines and their analogues, the stretching of electron gas to both sides of each terminal atom, has been calculated as 1.5\AA by H. Kuhn¹²¹, on the basis of vibrational treatment. As the length α on both ends is approximately 1.5\AA , this may be considered $\alpha \cong 1$. The value $\alpha = 1$ has already been used in the treatment of the dye molecule (XII^a). It has been found that the value of α is dependent on the end groups, and thus in a homologous series of dyes α is constant for all members of series. If strongly polarisable group in increasing order are introduced in the terminal atoms the value of α also increases. On the basis of above consideration the calculated values of $\lambda_{\text{-max}}$ of XII^a, XII^b with $J = 2, 3, 4, 5, 6$ and 7 are in excellent agreement with the experimental data of these carbocyanines¹¹⁸.



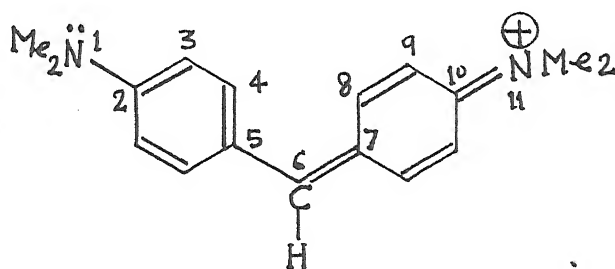
If the central CH group and N atoms are interchanged in the conjugated chain of the dye molecule, the shift in the λ -max does not take place which depends upon the electronegativity of hetero atom. When the chain length is increased by the inclusion of an additional $-CH=CH-$ group and the central CH is replaced by a N atom, a shift towards a longer wavelength region is expected. In general when replacing central CH group by a N atom, a shift towards shorter wavelength takes place if an even number of double bonds (J) is present between the two terminal N atoms; and an opposite shift will take place when J is an odd number. The above considerations may be expressed on a quantitative basis. A perturbational treatment of the problem

shows that the displacement of E of a given energy level produced by exchanging central C for N is given by following expression (11).

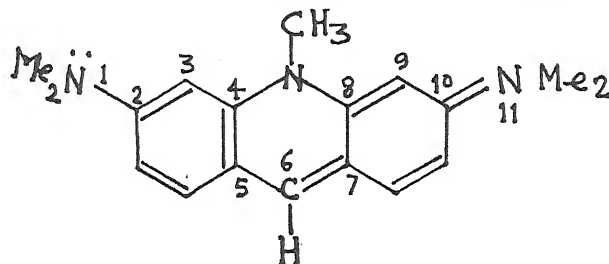
$$E = -A\psi \quad \text{----- (11)}$$

where A is a constant characteristic for a hetero atom, its value increases with the electro negativity of that atom, is the value of the normalised wave function at the hetero atom.

Let us now consider a few other classes of dyes which can not be treated by a simple free electron model molecular orbital treatment as discussed hither to. To illustrate this point Michler's hydrol blue (VI) and acridine orange (XIII) are discussed here. Both compounds possess a branched system of conjugated double bonds, and thus the π electrons can be described as standing waves in the coulomb field of a branched skeleton.



VI (Michler's Hydrol Blue)



XIII (Acridine Orange)

In the case of Michler's Hydrol Blue it has been assumed for the sake of simplicity that the branches indicated by thin lines in VI can be neglected, consequently the dye has been treated as an unbranched system of six pairs of π electrons. Similarly acridine orange may be treated in an analogous manner resulting in a system of seven pairs of π electrons moving in a molecular skeleton branched as indicated by heavy lines (XIII). Both the dyes possess the same dimethyl amine end groups, hence it can be assumed in both the cases that the π electron gas is extended by $\alpha \cdot 1 = 0.55 \times 1 = 0.77 \text{ \AA}^0$ to, either side of both terminal N atoms. The value of $\alpha = 0.55$ was obtained by introducing the experimental value of absorption maxima, $\lambda\text{-max} = 603 \text{ nm}$ in equation (10) (page 36). H. Kuhn has calculated the shift, $\lambda\text{-max XIII} - \lambda\text{-max VI}$ produced by acridine bridge formation, in the same manner as in the cases considered above. The value, $\lambda\text{-max XIII} = 471 \text{ nm}$ and the difference $\lambda\text{-max XIII} - \lambda\text{-max VI} = -132 \text{ nm}$ have been obtained. The experimental value of the shift caused by the formation of acridine bridge is, $\lambda\text{-max XIII} - \lambda\text{-max VI} = (491 - 603) = -112 \text{ nm}$ (hypsochromic shift) in agreement with the theoretical value. Upon increasing the electronegativity of the atoms at 6 and 12 in (XIII) the energy level of the highest occupied state will remain unaffected while the level of first excited state will be lowered resulting in the shift of the maxima to the longer wave region.

On the basis of above consideration the spectral changes, such as, bathochromic shift observed by replacing the

N-CH₃ group at position 12 in XIII with more electronegative oxygen atom and the bathochromic shift, that is produced on exchanging at position 6 the CH for C-C₆H₄-COO⁻ group or N, can well be explained at least in a qualitative manner.

H. Kuhn has used the branched Pi-electron gas model to treat other dyes in the same manner and the concept of branching leads to a simple explanation of even such characteristic compounds as the deep colour of the low molecular weight Wurster's blue and Azulene¹²².

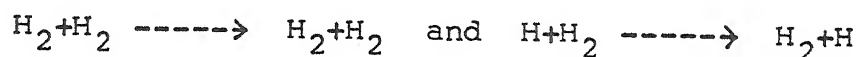
The FEMO theory was further refined by Labhart¹²³ who introduced the interaction between π electrons and elastic sigma skeleton. He was able to show that even for very long Polyenes a difference in single and double bond length of the same order of magnitude as in shorter Polyenes was to be expected. Olszewski¹²⁴ used a linear free electron model with electron-electron and electron core interaction for the calculation of:

- (i) lowest excited singlet triplet separation in Polyenes,
- (ii) twisting frequencies of ethylene and
- (iii) location of absorption maxima in cumulenes.

He also calculated the absorption maxima in the spectrum of symmetrical cyanine dyes and Polyenes by ASFEMO (Anti symmetrized free electron molecular orbital) method. An improvement of the theoretical λ -max values for cyanines was obtained by introducing 'resonance' barrier¹²⁵ in the free electron model.

Spectra of cyanine dyes and cata-condensed hydrocarbons were also analysed by Araki and Huzinaga^{126,127}, Basu¹²⁸, Dey¹²⁹ and by Rout et.al.¹³⁰ who employed suitably modified FEMO method.

A part from the spectral analysis, the refined FEMO has also been used for the calculation of optical rotatory power of Organic molecules. The model gave a method for the rapid evaluation of electric and magnetic transition moments and was further used for a better understanding of the skew conformation of butadiene. Shuler¹³² used the free electron model for calculating stability constants and absorption spectra of molecular complexes. Mueller¹³³ examined theoretically the bimolecular exchange reaction:



Via activated complex by the free electron model. Bonham et.al.¹³⁴ and Basu¹³⁵ treated the electrophilic substitution in aromatic molecules by the simple FEMO method. Their treatment is based on the fact that any aromatic substitution reaction proceeds through the formation of an activated complex. Nathan¹³⁶ employed successfully the FEMO method for the theoretical investigation of, diamagnetism of aromatic hydrocarbons.

TWO DIMENSIONAL MODEL :

The two dimensional free electron gas model^{137,138}, applied to the case of molecules with branched electron gas¹³⁹

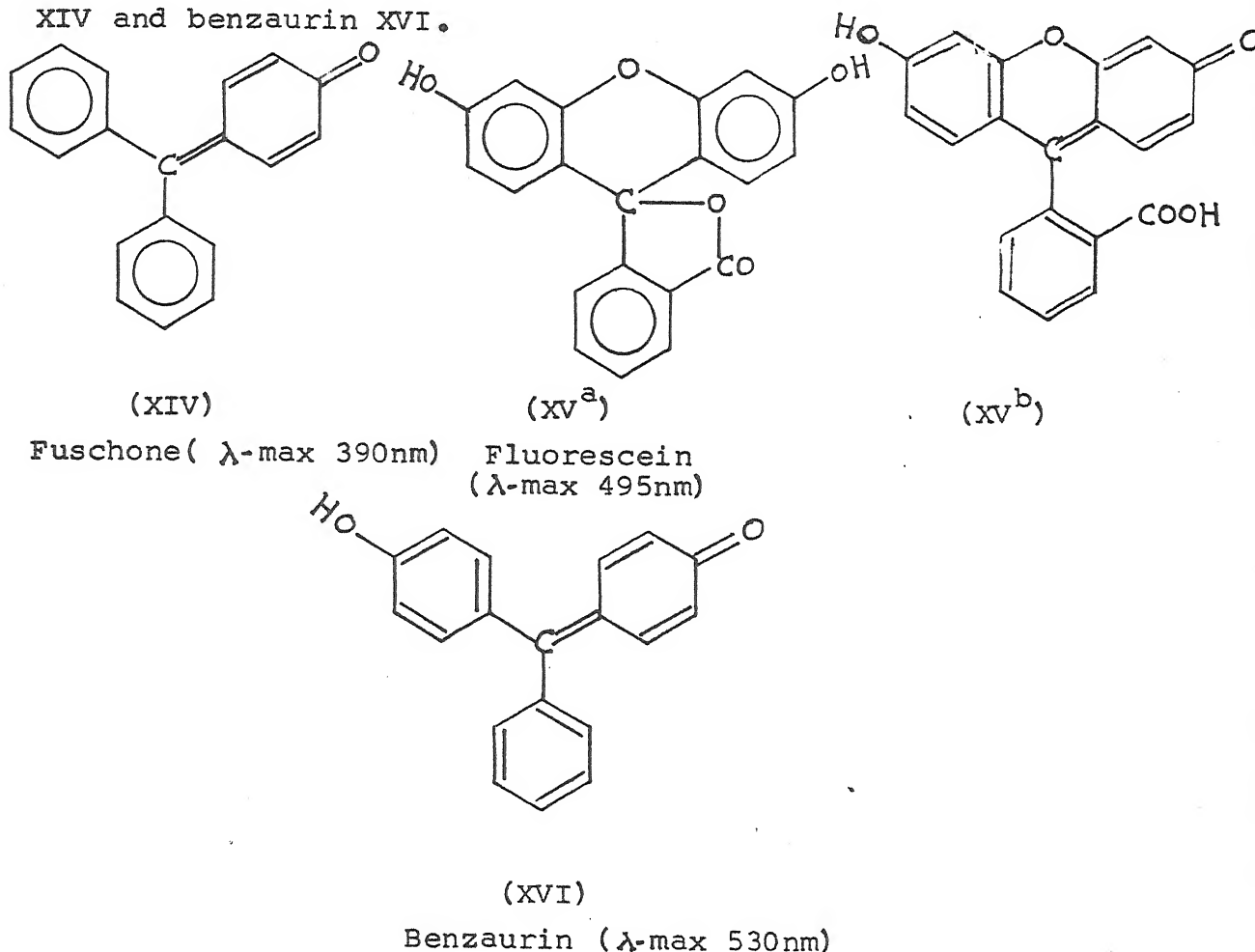
is closely related to the branched electron gas model described previously. Each state of interest in the two dimensional model corresponds to a state in the one dimensional model. In the two dimensional free electron gas model^{137,138} for a system with resonating structure, the plane of the centre of the atoms is chosen as the xy plane of a xyz co-ordinate system. It is assumed that the π electrons are in a potential field $V(z)+V(x,y)$, where $V(z)$ is a certain function of z . $V(xy)$ is the potential of a π electrons averaged over z and is the sum of the contribution of C atom. The contribution of a C atom can be obtained by nuclear charge and shielding considerations. The z part of the wave function of an electron in the potential $V(z)+V(x,y)$ can be separated from the xy part, and the problem of finding eigen functions $\psi_n(x,y)$ and eigen values E_n of the Schrodinger Equation-

$$\frac{\partial^2 \psi_n}{\partial x^2} + \frac{\partial^2 \psi_n}{\partial y^2} + \frac{8 \pi^2 m}{h^2} [E_n - V(x,y)] \psi_n = 0$$

can be solved by using an analog computer. The two dimensional treatment can be applied to Polyenes and Polyacetylenes. Using the observed values of bond distances, the position of the strong absorption bands were calculated and the results were found to be in good agreement with those of the one-dimensional treatment and with observed data¹⁴⁰. The two dimensional model may also be applied to dye molecules of any complicated shape.

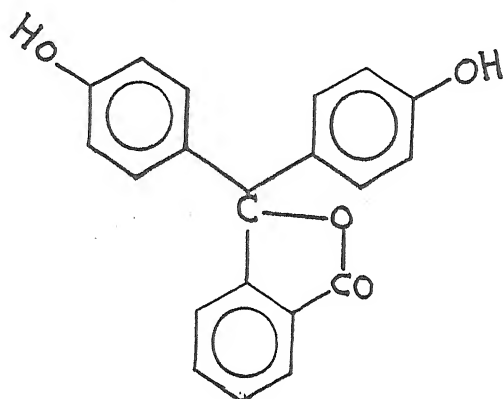
COLOUR AND CHEMICAL CONSTITUTION OF
PHTHALEIN AND SUCCINEIN DYES :

If N-CH₃ group at position 12 of acridine Orange(XIII) is changed by the more electronegative oxygen atom and H atom at position 6 is also replaced by -C₆H₄-COO⁻ entirely different series of dyes are obtained, which are known as Phthaleins XV^a, XV^b and XVII. Phthalein dyes are the derivatives of Pyronine dyes and they may be considered intermediate between fuschone XIV and benzaurin XVI.



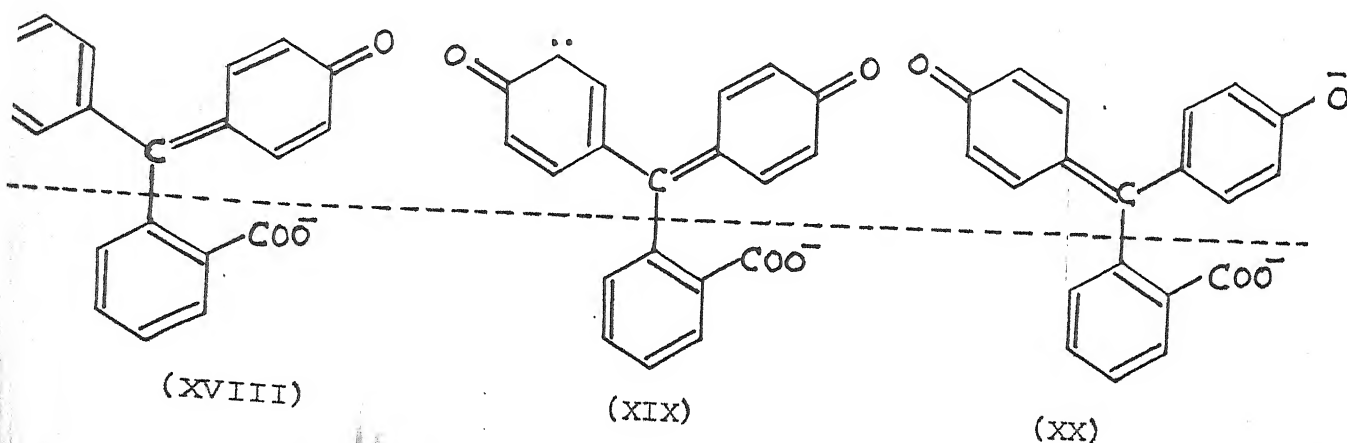
Phthalein are acid dyes where anion is the more important part, responsible for the colour of these dyes.

Phenol phthalein, a well studied representative of the series has a lactone structure XVII in neutral medium. The colourless lactone structure undergoes ring opening in alkaline solution (PH. 8.4) to give intensely red divalent anion XVIII. This shows the longest wavelength band at 552 nm in water, with an extinction coefficient of 31,000.

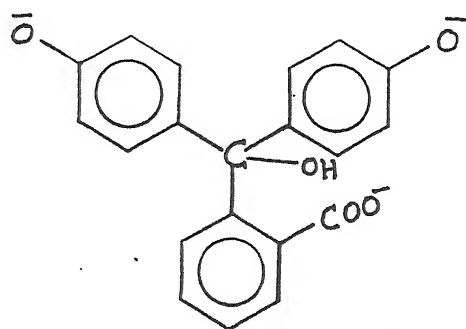


XVII (Phenolphthalein)

Red divalent anion form is actually responsible for the well known specific property of phenolphthalein as an indicator. Red divalent anion is actually a hybriide of XVIII & XX, two extremes and XIX and a number of its possible intermediate resonating structures:



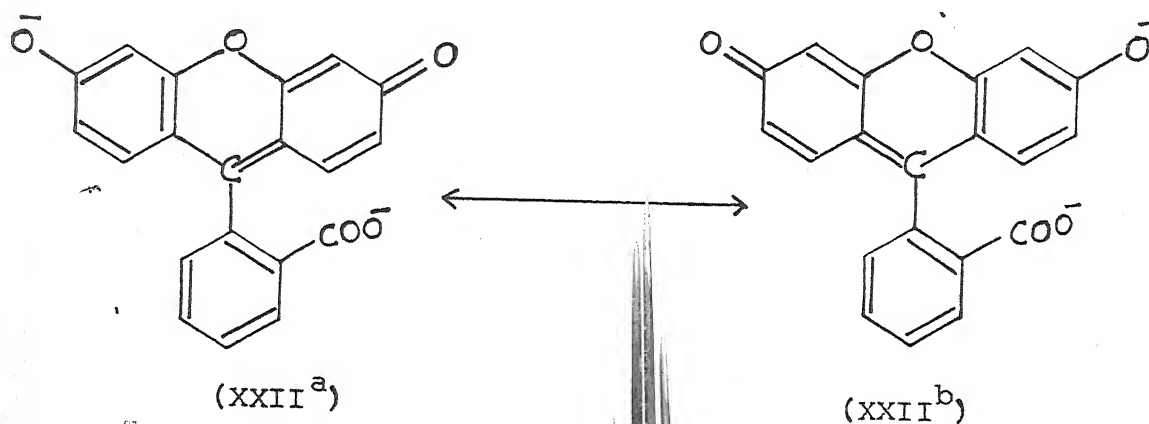
On addition of excess of alkali the divalent anion again becomes colourless and this is due to the formation of the colourless carbinol (XXI) a trivalent anion.



(XXI)

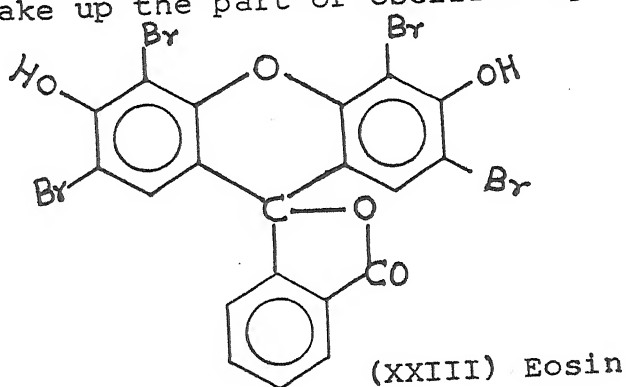
Trivalent anion
(a carbinol derivative)

Fluorescein XV^a is analogous to phenolphthalein, differing only in the presence of an oxygen bridge. Both Phenolphthalein and fluorescein in basic medium exhibit bathochromic shift of absorption band. In each case base produces an ion which can be represented by two equivalent resonating structures. Thus the base produces ions which are stabilised by resonance and this leads to absorption at longer wavelengths. Fluorescein has two equivalent resonating structures XXII^a and XXII^b in basic medium.



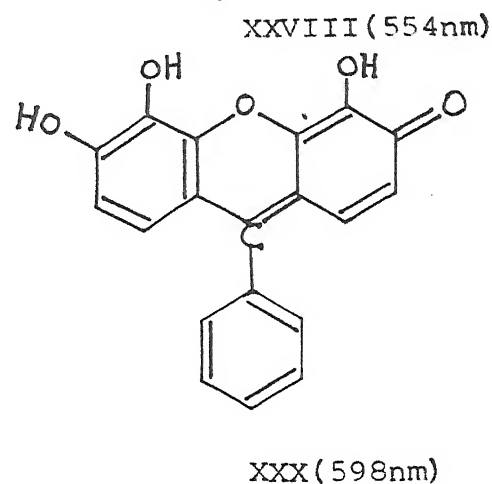
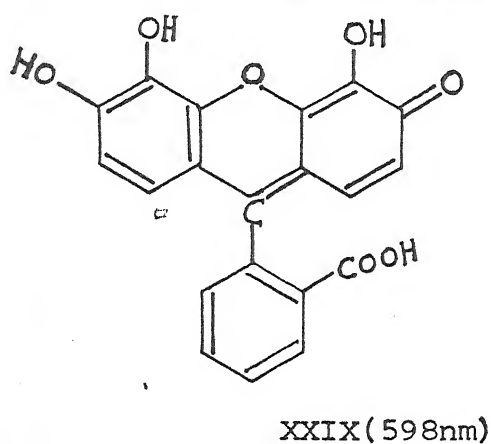
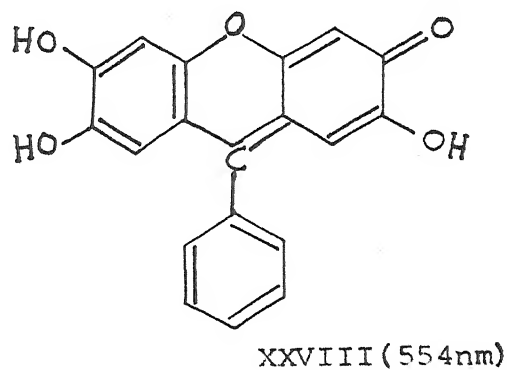
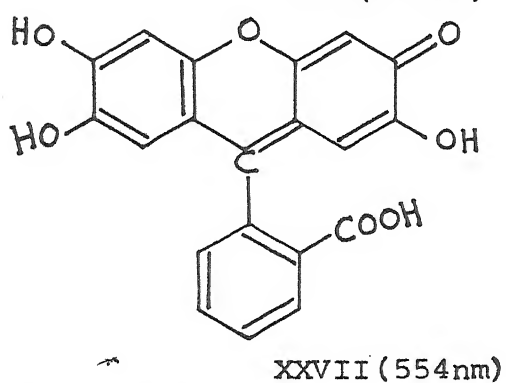
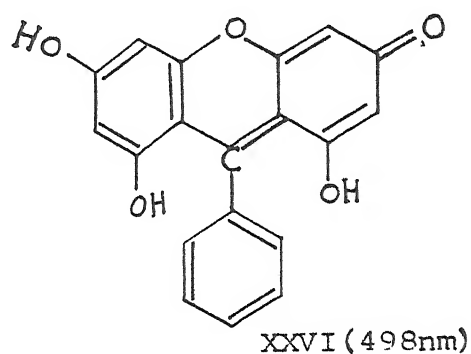
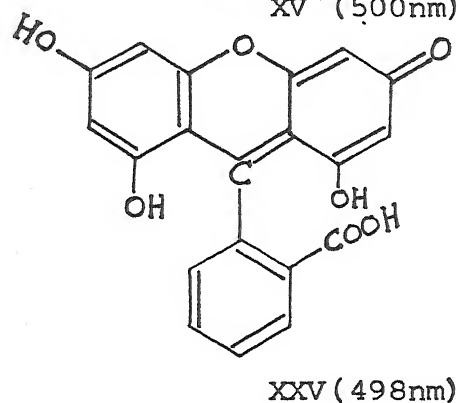
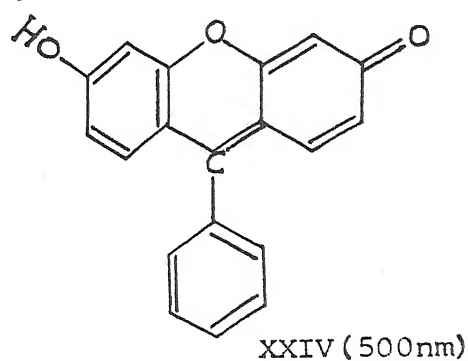
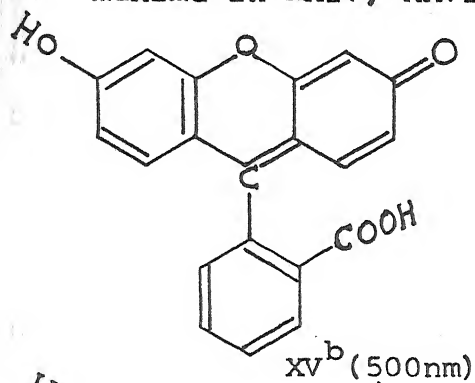
Fluorescein as expected absorbs at shorter wavelengths than the Phenolphthalein. The fluorescein anion is red (λ -max calc. 500nm in water), where as the Phenolphthalein anion is magenta (λ -max calc. 552nm in water). Fluorescein absorbs at shorter wavelengths because in it charge oscillation between two oxygen atoms is decreased due to oxygen bridge of Pyrone ring, which is capable to form a double bond with the ring acquiring some of the available charge. Fluorescein is characterised by its strong green fluorescence and may of its derivatives are also fluorescent.

Eosin (XXIII) having bromine atom in ortho positions to Pyrone oxygen, the electron density of carbon atoms of Pyrone ring is increased and consequently it hinders the oxygen to take up the part of oscillating charge.



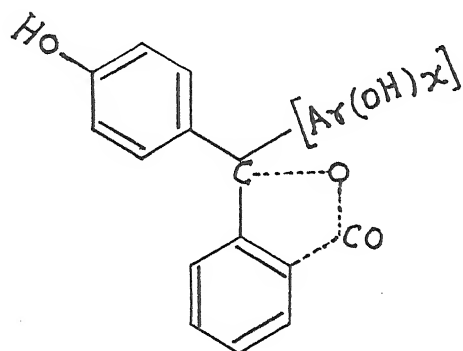
It is evident from the structures of Phthalein (XVIII), and also from above discussion that only that part of the molecule which is shown above the dotted line plays an important part in the light absorption as regards, the main absorption band of the molecule. The removal of the carboxyl group in compounds,

xv^b, XXV, XXVII, XXIX, does not affect the position of absorption maxima in XXIV, XXVI, XXVIII, XXX.



By making changes in the lower part (below dotted line) of the Phthalein molecule (XV^a and XVII) the effect on light absorption has been observed by a number of workers¹⁴¹⁻¹⁶⁵ but no significant change in λ_{max} has been reported which confirmed the previous observations.

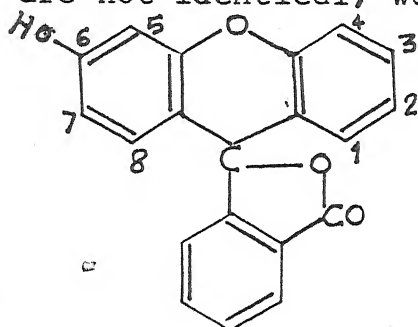
Phthaleins of the type XXXI in which the two aromatic hydroxy molecules are dissimilar have been prepared by Ghatak and Dutt¹⁶². Recently novel analogous of Phthaleins were also prepared by Gupta et.al.¹⁶³⁻¹⁶⁵ and Beg & Coworkers¹⁶⁶⁻¹⁶⁷.



(XXXI)

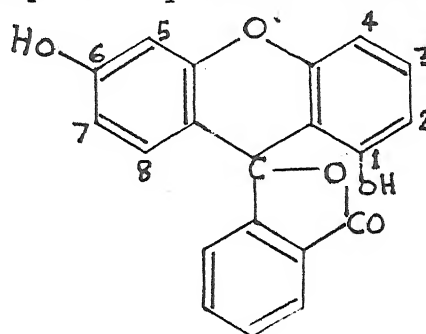
(Phthalo-Phenone derivative)

Further more interesting unsymmetric fluoresceins where the substituents in the two sides of the fluoran nucleus are not identical, were also prepared by above workers¹⁶².



(XXXIII)

6-hydroxy fluoran(493nm)



(XXXII)

1,5 dihydroxy fluoran

In the present thesis novel analogues of Succineins were also prepared by condensing various β -aroyl propionic acids with various phenols in presence of concentrated Sulphuric acid. Colour of these dyes was discussed in the next chapter.

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167. J.S. Parmar, Ph.D. Thesis, Bundelkhand University, Jhansi (1992).

CHAPTER- II

RESULT AND DISCUSSION

Attempts to make changes in the absorption of phenolphthalein molecule require changes to be incorporated either in upper or lower part of the molecule. It has been observed that alterations in the number, position, and nature of the auxochrome incorporated in the upper part of the molecule, which is its resonating part, results in a marked change in λ -max. Whereas, such changes in the lower part, the acid part, which does not partake in resonance bear no fruits. Further, the lactone form of phenolphthalein can be represented by two equivalent extreme quinonoid forms (XVIII & XX) in alkaline medium. If such a radical alteration could be accomplished in the molecule that replaced one of the hydroxy aromatic nuclei by an alkyl, aryl group or by a heterocyclic ring, the resonance in phenolphthalein nucleus would then be possible only in one of the two above mentioned quinonoid forms. Consequently, colour development of the substance will be expected to be much less intense than that in the case of phenolphthalein. To study this effect of the above planned alterations in the upper (non acid) part of the phthalein molecule, the following eleven α -keto acids (series A, B and C) were prepared and condensed with various phenolic compounds in order to get mixed phthaleins (phthal-as-eins).

To see the effect of lower acid part in the colour of the dye three β -aroyl propionic acids (series D) were also prepared and condensed with various phenolic compounds to get

mixed succineins (succin-as-eins). General structure of phthal-as-eins and succin-as-eins prepared are given by XXXIV-A and B respectively.

ACIDS OF SERIES - A :

- (1) O-(4-amino 3-chloro benzoyl) benzoic acid.
- (ii) O-(3-carbmethoxy 4-hydroxy benzoyl) benzoic acid.
- (iii) O-(2-hydroxy 5-methyl benzoyl) benzoic acid.
- (iv) O-(3,4-dimethyl benzoyl) benzoic acid.

ACIDS OF SERIES - B :

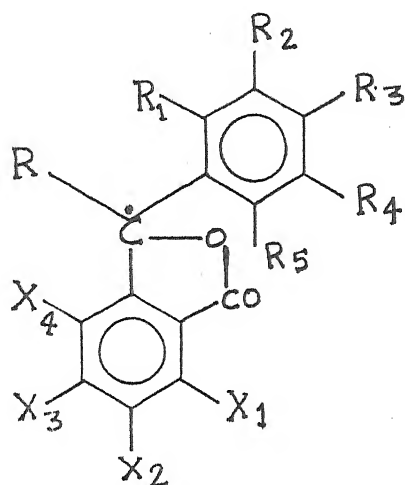
- (i) O-(4-amino 3-chloro benzoyl) tetrachloro benzoic acid.
- (ii) O-(3-carbmethoxy 4-hydroxy benzoyl) tetrachloro benzoic acid.
- (iii) O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid.
- (iv) O-(3,4-dimethyl benzoyl) tetrachloro benzoic acid.

ACIDS OF SERIES - C :

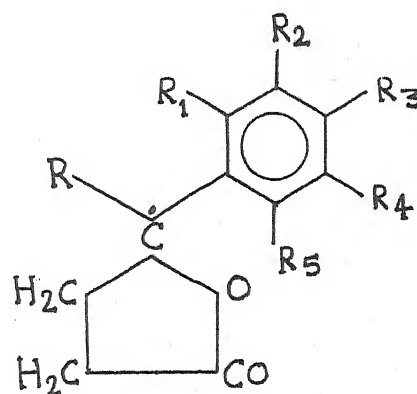
- (1) O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid.
- (ii) O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid.
- (iii) O-(3,4-dimethyl benzoyl) m-nitro benzoic acid.

ACIDS OF SERIES - D :

- (i) β -(4-amino 3-chloro benzoyl) propionic acid.
- (ii) β -(2-hydroxy 5-methyl benzoyl) propionic acid.
- (iii) β -(3,4-dimethyl benzoyl) propionic acid.

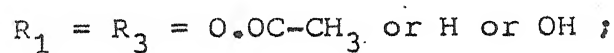
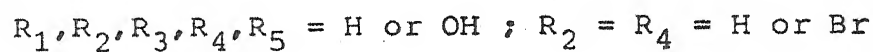
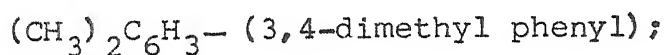
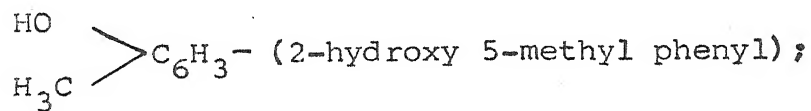
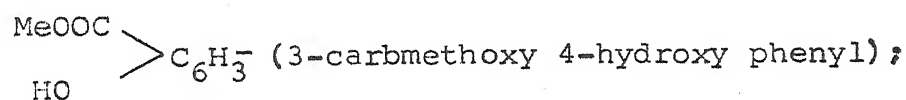
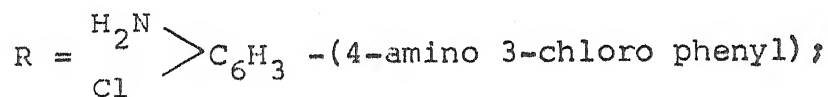


XXXIV-A
(Phthal-as-ein)



XXXIV-B
(Succin-as-ein)

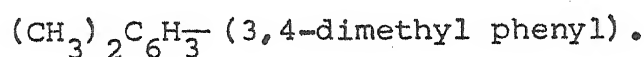
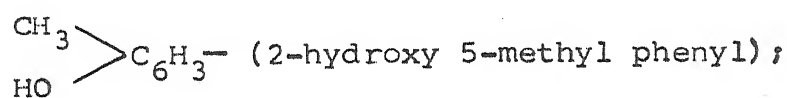
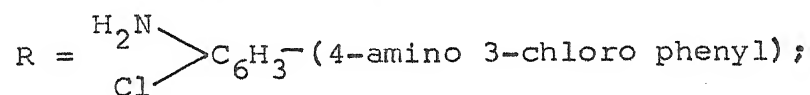
FOR DYES DERIVED FROM SERIES A AND B ACIDS :



$X_1 = X_2 = X_3 = X_4 = H$ (For dyes derived from series A acid).

$X_1 = X_2 = X_3 = X_4 = Cl$ (For dyes derived from series B acid).

FOR DYES DERIVED FROM SERIES C AND D ACIDS :



$R_1, R_2, R_3, R_4, R_5 = H \text{ or } OH; R_2 = R_4 = H \text{ or } Br.$

$R_1 = R_3 = O.OC-CH_3 \text{ or } H \text{ or } OH$

$X_1 = X_2 = X_3 = H ; X_4 = NO_2$ (For dyes derived from series C acids)

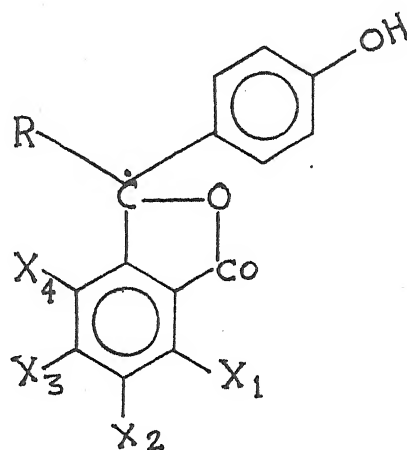
The nomenclature of these dyes has been arrived at by considering the unsymmetry in the structure of the molecule. These may be regarded as mixed or unsymmetric Phthaleins (XXXIV-A) as derivative of phthalide, and unsymmetric Succineins (XXXIV-B); for convenience and uniformity and owing to asymmetric Central Carbon Atom(\dot{C}) present in all, the more satisfactory nomenclature for XXXIV-A and XXXIV-B is adopted, and the compounds are named as follows:-

Phthal-as-eins, succin-as-eins, 'as' representing asymmetry; 'ein' representing the class of the dyes (phthalein or succinein).

STRUCTURE OF PHTHAL-AS-EINS :

PHENOL PHTHAL-AS-EINS :

On the basis of the study of the chemical constitution of these XXXIV-A dyes (discussed in the preceding section page 101) (XXXV) has been assigned to phenol phthal-as-eins.



(XXXV)

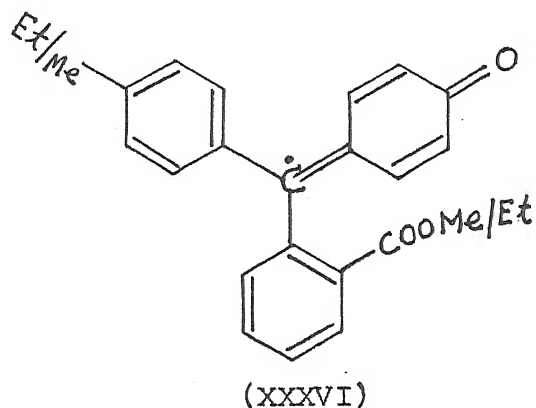
R = 4-amino 3-chloro phenyl; 3-carbomethoxy 4-hydroxy phenyl;
2-hydroxy 5-methyl phenyl; 3-4-dimethyl phenyl;

$X_1 = X_2 = X_3 = X_4 = \text{H or Cl}$

$X_1 = X_2 = X_3 = \text{H}; X_4 = \text{NO}_2$

It may be noticed that the assigned structure of phenol phthal-as-ein (XXXV), is similar to dimethyl¹ or diethyl² (XXXVI) derivative of phenolphthalein. In these derivative there seems the possibility of the same type of resonance to occur as exhibited

by phenolphthalein itself. In the same way, the resonance of phenolphthalein type will altogether absent in XXXV.



The analogues dimethyl derivative is orange red and the corresponding diethyl derivative is yellow even in the solid state.

SERIES - A :

The representative dyes of the series (A) i.e. -

- (i) (4-amino 3-chloro phenyl) phenol phthal-as-ein.
- (ii) (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein.
- (iii) (2-hydroxy 5-methyl phenyl) phenol phthal-as-ein.
- (iv) (3,4-dimethyl phenyl phenol) phthal-as-ein.

The above four dyes are buff, orange, pinkish red and brown in colour respectively.

SERIES - B :

The dyes of this series named -

- (i) (4-amino 3-chloro phenyl) phenol tetrachloro phthal-as-ein.
- (ii) (3-carbmethoxy 4-hydroxy phenyl) phenol tetrachloro phthal-as-ein.
- (iii) (2-hydroxy 5-methyl phenyl) phenol tetrachloro phthal-as-ein.
- (iv) (3,4-dimethyl phenyl) phenol tetrachloro phthal-as-ein.

The above four dyes are orangish brown, orange, reddish orange, pink in colour respectively.

SERIES - C :

The dyes of this series named -

- (i) (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein.
- (ii) (2-hydroxy 5-methyl phenyl) phenol nitro phthal-as-ein.
- (iii) (3,4-dimethyl phenyl) phenol nitro phthal-as-ein.

The above three dyes are blackish brown, brown and light brown in colour respectively.

SERIES - D :

The dyes of this series named -

- (i) (4-amino 3-chloro phenyl) phenol succin-as-ein.
- (ii) (2-hydroxy 5-methyl phenyl) phenol succin-as-ein.
- (iii) (3,4-dimethyl phenyl) phenol succin-as-ein.

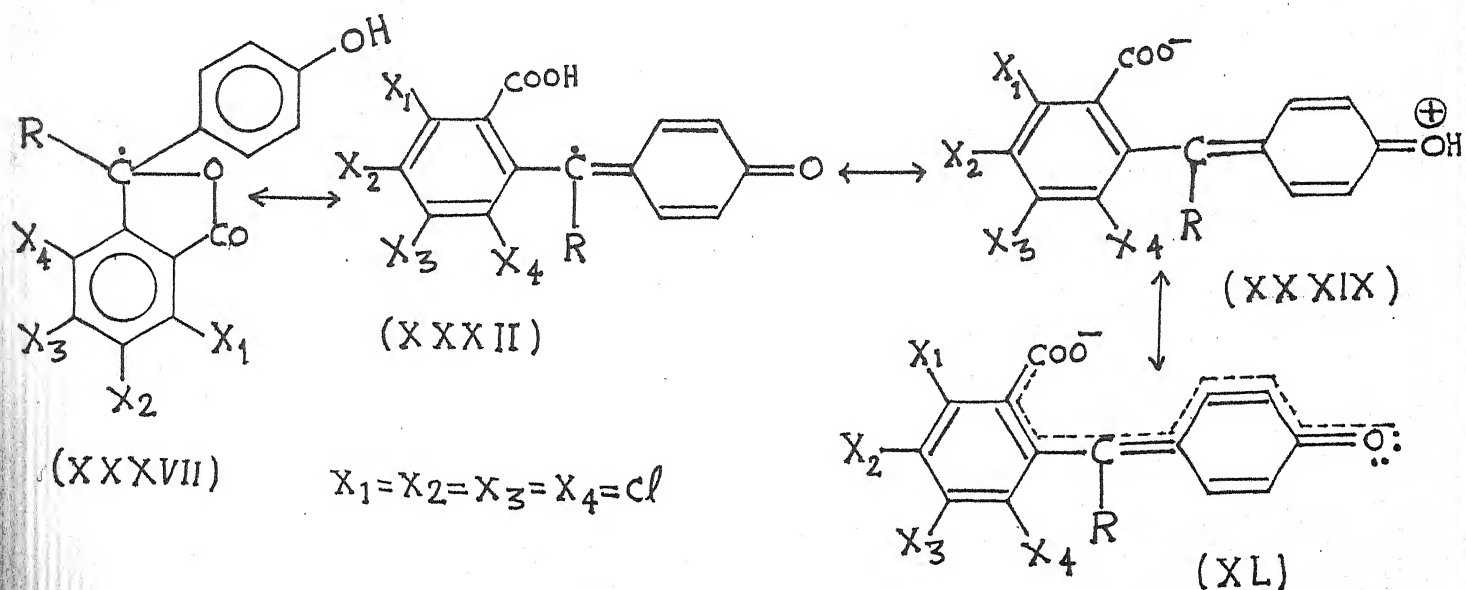
The above three dyes are brown, dark brown and dark

brown in colour respectively.

The colour of these phenol phthal-as-ein in neutral as well as in alkaline medium and their λ -max values are given on page (79-80) as well as in tabular form at the end of the thesis.

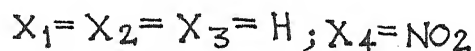
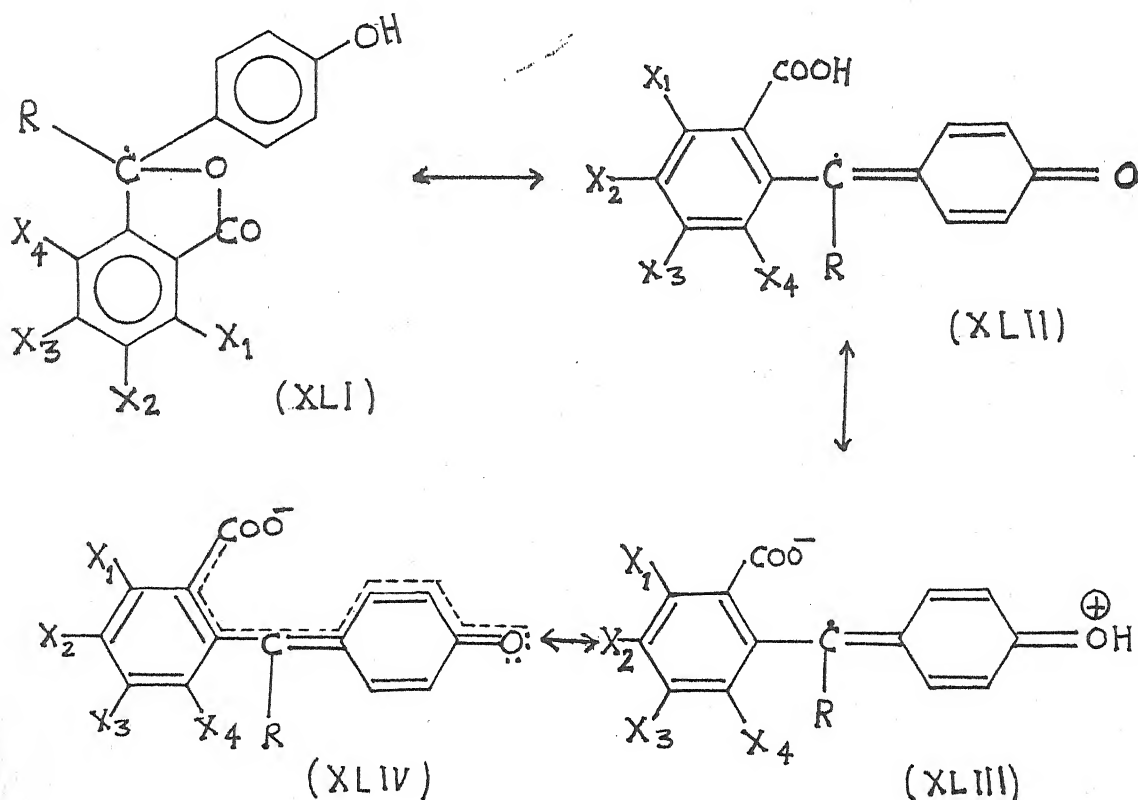
The colour of phenol phthal-as-eins may be explained as already discussed and interpreted in the case of phenolphthalein. (Chapter I page 44).

The colour of phenol tetrachloro phthal-as-eins may be explained on the basis of resonance occurring among various neutral (XXXVII and XXXVIII) and polar (XXXIX and XL) structures of the molecule. Due to ^{the} occurrence of the resonance in the molecule, the presence of quinonoidal conjugation becomes possible in different partaking structures and at the same time the formal charge is created in the polar resonating states in the basic medium. A symmetry of phenolphthalein is altogether absent here but possibly the charge travels through the dotted lines (XL) and the absorption maxima is almost the same as that of phenolphthalein (XVIII-XX) in moderate basic medium.



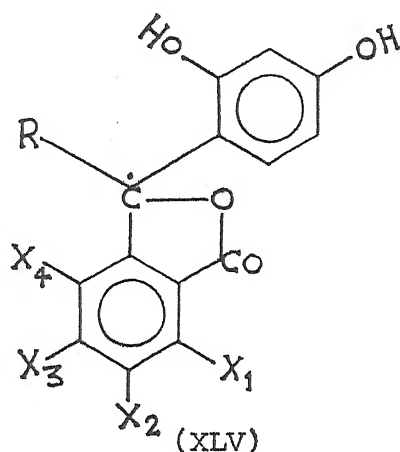
The phenol tetrachloro phthal-as-eins studied here exhibit similar behaviour in basic medium as phenolphthalein. The monovalent anion of phenolphthalein is a colourless derivative, while the divalent anion (XVIII and XX) gives pink colour but the trivalent anion (XXI) is again colourless. In the same way the present phenol tetrachloro phthal-as-eins described in the thesis give violet colour in moderate basic medium and the disodium salts become almost colourless. The divalent colourless anions with strong acids show again enhancement of colour (XXXIX).

Similarly the colour of phenol nitro phthal-as-eins incorporated in the thesis, may also be explained by considering the neutral (XLI and XLII) and the polar (XLIII) and (XLIV) resonating structures for the molecule.

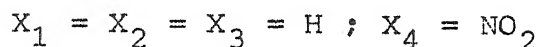
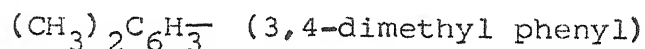
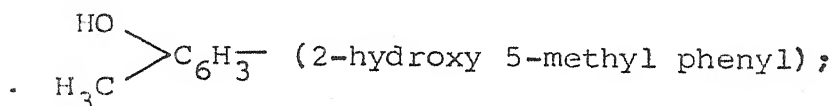
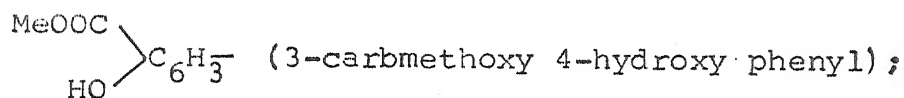
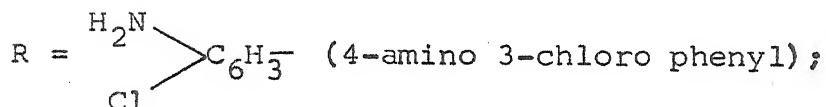


THE RESORCINOL PHTHAL-AS-EINS :

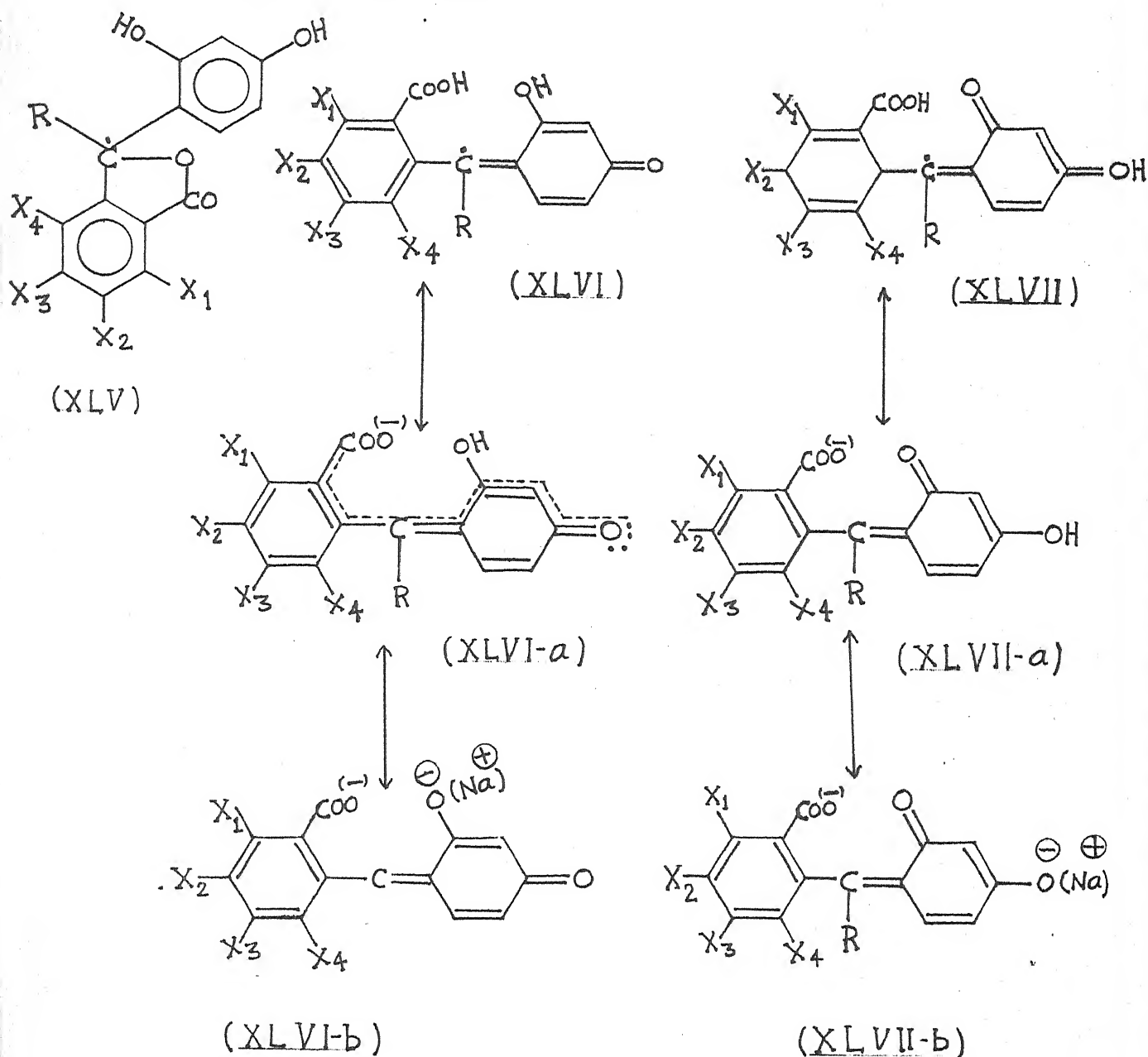
The colour of the resorcinol phthal-as-ein (XLV) may be explained in relation to their chemical structures (discussed in preceding section, page 101 . On the basis as already described in the case of phenol phthal-as-eins.



Resorcinol phthal-as-ein.



In resorcinol phthal-as-eins, there are two hydroxy groups (2:4 positions) instead of one hydroxy group (4 position) in the phenolic part of the molecule (XXXV). Out of the two hydroxy groups, one acts as a chromophore to produce conjugation while the other hydroxy group acts as an auxochrome, hence even the neutral molecule can possibly exist as a resonance hybrid of the following structures.



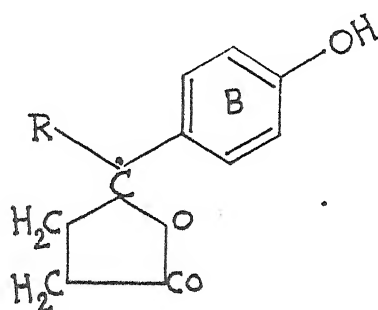
Thus the colour of resorcinol phthal-as-eins is well accounted for either in solid state (yellow, yellowish-orange, reddish orange, yellowish brown, brown) as well as in neutral medium (λ -max 455-480nm). However, by the addition of alkali the polar forms (XLVIA, XLVIIa, XLVIB and XLVIIb) of the molecule are produced resulting in increase in the number of resonating structures of the molecule. This increase is responsible for producing more crowded and depressed energy levels, consequently a bathochromic shift in λ -max takes place. Actually all these dyes have absorption bands at 450-480nm (in neutral medium), while in slightly alkaline medium λ -max values in between 490-520nm have been observed.

THE POLYHYDROXY PHENOL PHTHAL-AS-EINS :

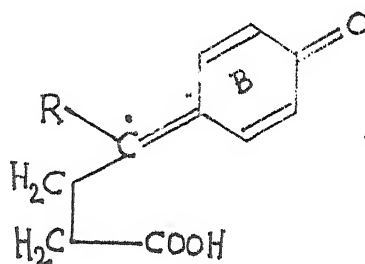
In most of the poly hydroxy phenol phthal-as-eins one hydroxy group takes part as chromophore and rest of the hydroxy group(s) present, may be acting as auxochrome(s) causing deepening of the colour of these dyes (appearance varies from yellow to dark brown etc.). In some cases these dyes eg. hydroquinone, catechol, phloroglucinol and pyrogallol phthal-as-eins have been found to decompose in alkaline solution. Due to this decomposition of dyes a reliable absorption maxima could not be determined, hence it is difficult to put forward a satisfactory explanation for their colour.

COLOUR OF SUCCIN-AS-EINS AND λ -MAX CALCULATION :

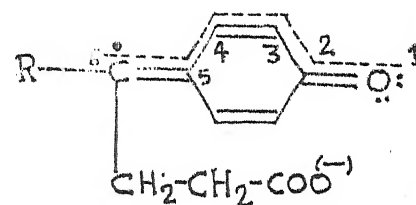
The λ -max values for various types of succin-as-eins have been observed by some workers and it falls between 385-430nm. In the present thesis succin-as-eins were prepared from three β -aroyl propionic acids (given on page 63). The various aryl phenol succin-as-eins are represented by the following resonating structures (XLVIII, XLIX, L) which also explained their colour and λ -max (420-440nm) here R = substituted phenyl. Structure (L) makes a real contribution in an alkaline medium. The dotted line indicates the possibility of travelling the electron along the conjugated chain.



(XLVIII)

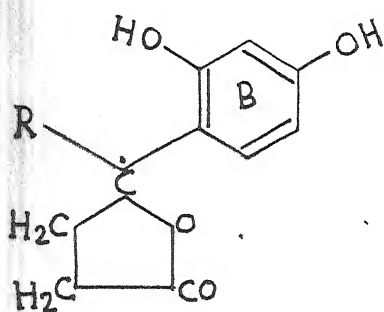


(XLIX)

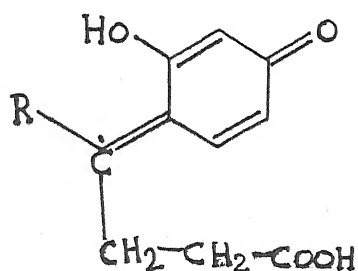


(L)

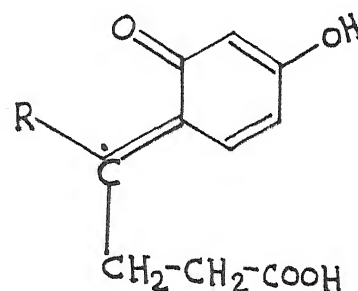
In this case it is not possible for conjugation to extend beyond the chiral carbon atom present at position six (6th) and the pi-electron gas consists of eight electrons for four pi-bonds (i.e. $J=4$), out of which six electrons are contributed by three double bonds and two electrons by charge free oxygen atom \ddot{O} (i.e. 4 pi-bonds are contributed in coulombic field). Stretching of electron gas is not possible at



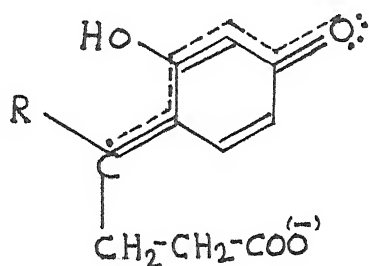
(LI)



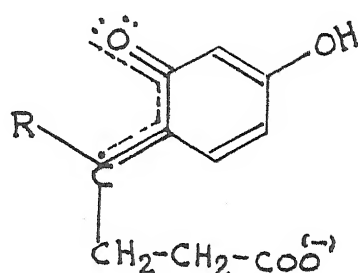
(LII)



(LIII)



(LIV)



(LV)

In this case o-quinonoid structures (LIII) and (LV) make much more contribution than p-quinonoid structure (LII and LIV) and due to auxchromic effect of OH group meta to quinonoid oxygen it shows the λ -max value (480-500nm) in the range of phthal-as-eins.

It may be well concluded from the forgoing discussion about the different theories of colour of dyes in relation to their chemical structure (chapter I) that no single theory seems capable of explaining and predicting the colour quite accurately. Inspite of the above observation, the FEMO gas

model has been found a better fit theory than others. There might arise a few mathematical complexities in the application of the two dimensional free electron gas model. As for as rigorous assumptions are concerned all the theories VB, MO and FEMO require these, without which it would be impossible to make any calculation even for very simple molecules.

CALCULATION OF ABSORPTION MAXIMA OF PHTHAL-AS-EIN DYES :

The theoretical values of absorption maxima of phenol phthal-as-eins may only be calculated by making rigorous approximation for the pi-electron gas model (equation 10, page 36). Here each dye molecule is unsymmetric, hence two equivalent extreme structures with formal charge like phenolphthalein or fluorescein are not possible. Thus unsymmetric extended conjugated chains with formal charge at one end only, may be present in all the resonating forms, contributing to the dye molecule. Therefore, for calculation major contributing structures (XL) and (XLVIa) are to be considered. Here in all, ten electrons are regarded to take part in the formation of pi-electrons gas, eight pi-electrons of the four pi-bonds and two pi-electrons from the charge free \ddot{O} : (neutral oxygen atom). The effective conjugated chains have been depicted by dotted lines and for simplification the lower portion is neglected by making approximations which does not vitiate the result. Thus five pi-electrons gas are possible which are responsible for the creation of coulomb force along the polar molecule with formal charge. To consider

the stretching beyond the two ends of the conjugated chain, here it is possible only at one end = $\ddot{O}:$. The value $\alpha = 0.33$ has been derived from the observed λ -max value of benzaurine dye (XVI page 43) with oxygen end groups. Thus by applying the equation 10 (page 36).

$$\begin{aligned}\lambda_{\text{max}} &= 127 \frac{(J + \alpha/2)^2}{(J + 3/2)} \\ &= 127 \frac{(5 + 0.33/2)^2}{(5 + 3/2)} \\ &= 127 \frac{(5.165)^2}{6.5} \\ &= 520\text{nm (approx.)}\end{aligned}$$

This value may be regarded in excellent agreement with the observed values of phenol-phthal-as-eins (530-560nm) and for resorcinol phthal-as-eins (490-520nm).

It has not been possible to apply the free electron molecular orbital treatment in the case of polyhydroxy phenol phthal-as-eins due to the unmanageable difficulties, presented by their structural complicacies, to derive simplified expression for the calculation of their absorption maxima.

H. Kuhn³⁻⁴ has further given a refined treatment on the basis of 'one dimensional wave shape potential model' which is applicable for completely symmetrical type of dye. A still better

treatment on the basis of 'two dimensional electron gas model' has been proposed by the same author⁵ and it is claimed that this may be applied to dye molecule of any complicated shape but the problem of mathematical calculations is very discouraging and it can not be done without the help of computer. Due to the lack of these facilities the refined treatment could not be applied here.

The various phenol phthal-as-eins prepared i.e. (4-amino 3-chloro phenyl) phenol phthal-as-ein; (3-carbomethoxy 4-hydroxy phenyl) phenol phthal-as-ein; (2-hydroxy 5-methyl phenyl) phenol phthal-as-ein; (3,4-dimethyl phenyl) phenol phthal-as-ein, are buff, orange, pinkish red and brown in colour. The bathochromic shift is quite significant in these phenol phthal-as-eins in alkaline medium. Their λ -max values in neutral and in alkaline mediums are (520-530nm), (460-500nm), (510-530nm) and (520-545nm) respectively.

The colours and λ -max values in neutral and alkaline medium of the dyes (4-amino 3-chloro phenyl) phenol tetrachloro phthal-as-ein; (3-carbomethoxy 4-hydroxy phenyl) phenol tetrachloro phthal-as-ein; (2-hydroxy 5-methyl phenyl) phenol tetrachloro phthal-as-ein; (3,4-dimethyl phenyl) phenol tetrachloro phthal-as-ein; (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein; (2-hydroxy 5-methyl phenyl) phenol nitro phthal-as-ein; (3,4-dimethyl phenyl) phenol nitro phthal-as-ein; are orangish

brown (λ -max 520-545nm); orange (λ -max 460-510nm); reddish-orange (λ -max 480-520nm); pink (λ -max 510-535nm); blackish-brown (λ -max 520-545nm); brown (λ -max 520-535nm) and light brown (λ -max 510-530nm) respectively.

These dyes are colourless in neutral medium and in basic medium (on adding a drop of 2% caustic soda solution) gave violet colour.

The above λ -max values observed are in good agreement with the λ -max values found for analogous phenol phthal-as-eins.

1. Phenol phthaleins (λ -max 550nm in alkaline medium).
2. Phenol tetrachloro phthaleins (λ -max 585nm in alkaline medium).
3. Phenol nitro phthaleins (λ -max 560nm in alkaline medium).

The higher λ -max values observed in the case of some phenol tetra chloro phthal-as-eins and phenol nitro phthal-as-eins may be due to the presence of amino and hydroxyl auxochromes in phenyl ring. These groups may be responsible for the enhancement of the colour. Partly nitro groups in the acid part in nitro phthal-as-eins and chlorine atoms in the acid part in tetrachloro phthal-as-eins may be responsible for the enhancement of the λ -max values and the colour of the dyes.

In various resorcinol phthal-as-ein dyes prepared, the λ -max (460-480nm) in neutral and 490-520nm in alkaline medium) is lower than λ -max values observed in various phenol phthal-as-

-ein dyes prepared. A possible explanation for this observation may be that in resorcinol phthal-as-ein dye (XLV, page 71), there are two hydroxy groups (2:4 positions) instead of one hydroxy group (at 4 position) in phenol phthal-as-ein dyes structure (XXXV, page 66). In one of the main contributing structures of the molecule the conjugation is blocked beyond the 2-hydroxy group (XLVIa) and consequently the length of conjugated chain is decreased. This shortening of conjugated chain (structure XLVIIa, page 72) may be held responsible for lowering of the λ -max in these compounds.

All the resorcinol phthal-as-eins studied here have absorption maxima (460-480nm) in neutral medium and (490-520nm) in moderate alkaline medium. Values of absorption maxima for these resorcinol phthal-as-ein dyes have been given in tabular form in the end of the thesis.

In the case of Novel analogues of succineins the λ -max values have been observed for the resorcinol dye i.e. (4-amino 3-chloro phenyl) resorcinol succin-as-ein; (2-hydroxy 5-methyl phenyl) resorcinol succin-as-ein; (3,4-dimethyl phenyl) resorcinol succin-as-ein. The colour of these dyes and their λ -max values observed are orange (λ -max 460-500nm); brown (λ -max 520-535nm) and dark brown (λ -max 510-545nm) respectively. These λ -max values are in good agreement with the reported arylated resorcinol succin-as-eins.

1. The significant difference between phthalein dyes (Pyronine dyes) and phthal-as-ein dyes (described in the thesis) may be observed that while considering the different charged structures to explain their respective colour or to calculate the theoretical value of λ -max, in the first case the acid part below the dotted line (page 44) is not considered at all while in the second case the acid part is involved and is capable to produce a number of charged structures which are responsible for their colour.

2. Practically there is no significant effect of different substituents in the aromatic ring of the acid part but it may be observed that the phthal-as-ein dyes derived from the γ -keto acids having 4-amino 3-chloro phenyl; 3-carbomethoxy 4-hydroxy phenyl; 2-hydroxy 5-methyl phenyl; 3,4-dimethyl phenyl, substituted on the lactol carbon (central carbon atom) show a little more bathochromic shift. As already explained it might be due to these very substituents mentioned above.

3. The distinguishing feature of two classes of dyes (phthal-as-ein (XXXIV-A) and succin-as-ein (XXXIV-B) are that structure (XXXIV-A) contains phthalide (aromatic lactone system) where as structure (XXXIV-B) contains butyro lactone system.

When the quinonoid forms of two class of dye i.e. (XL) and (L) are compared, it is observed that in the case of phthal-as-ein (XL) the conjugation is extended between oxygen atom.

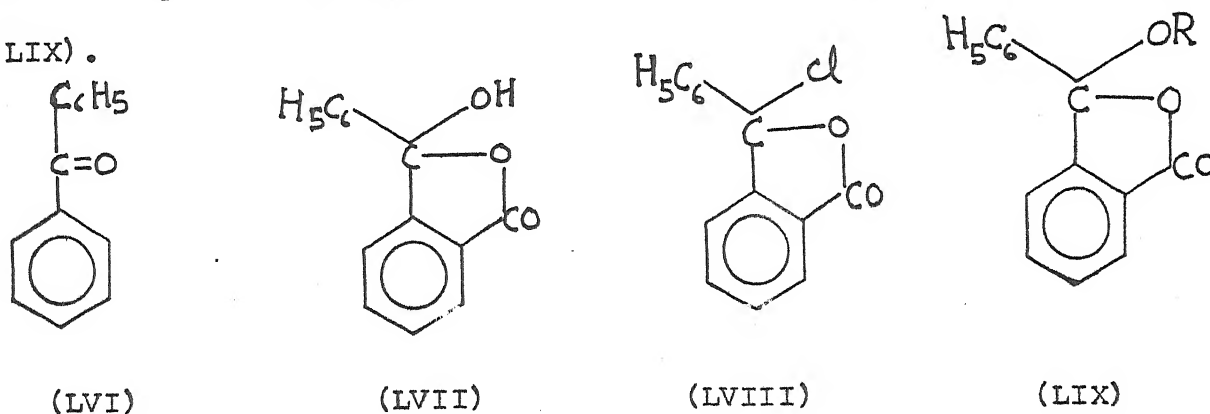
present in ring (B) at position 1 to position 8 to ring (C) beyond the chiral carbon atom present at position (6), which is not possible in the case of succin-as-ein (structure L), even then λ -max values of two classes of dyes fall within the same region. The high value for λ -max for succin-as-ein has already been explained, that the ortho quinonoid form makes much more contribution than the para quinonoid form and the auxochromic effect (due to OH group) enabled the structure to show λ -max value in the range of phthal-as-ein.

4. Though no one single theory is able to explain and predict the colour and absorption maxima of all types of dyes still the FEMO gas model theory is best at present to calculate and predict the colour and absorption maxima after making some assumptions which do not vitiate our problem at all. In the present thesis, FEMO gas model has been very successfully applied where the calculated values are quite in excellent agreement with the observed values (λ -max).

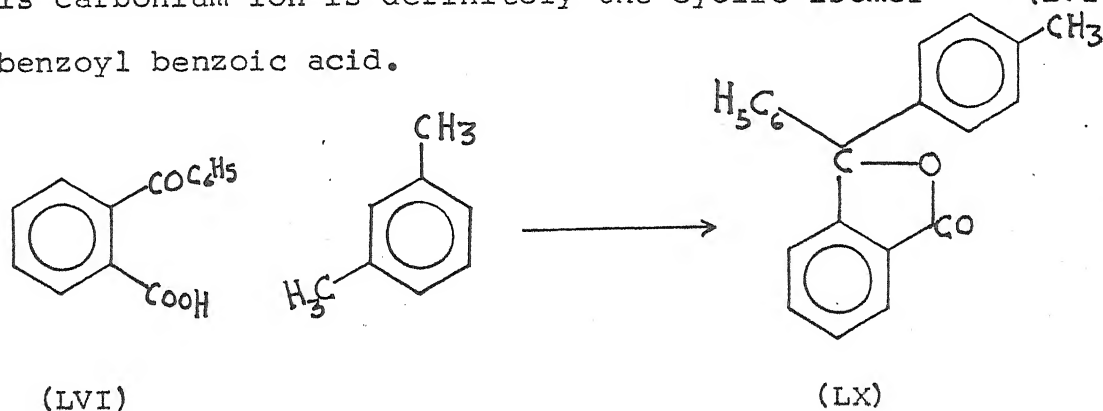
CHEMICAL CONSTITUTION OF PHTHAL-AS-EIN DYES :

The open chain substituted or un substituted γ -keto acids possess a characteristic structural requirement due to which they are capable of existing in cyclic tautomeric form also. The formation of ring tautomer (lactole form⁶) takes place due to electrophilic ring-chain tautomerism where the electrophile is proton (hydrogen). Amount of the lactol depends

on the extent of this prototropic change. Generally it has been observed that γ -keto acids exist chiefly as lactol or equilibrium mixture of ring and chain tautomers⁷⁻⁸. The lactols give well crystalline acetyl derivatives, still retaining their cyclic structures. Therefore, it is obvious that the cyclic tautomer is comparably more stable form than the chain tautomer⁹⁻¹². The formation of Pseudoesters¹³ of O-benzoyl benzoic acid (LVI) has been proposed on the basis of cyclisation to lactol (LVII) which can yield a pseudochloride¹⁴ (LVIII). This pseudochloride on heating with appropriate alcohol yields corresponding ester (LIX).



Formation of compound (LX) from O-benzoyl benzoic acid and meta xylene catalysed by per chloric acid has been proposed through the 3-phenyl phthalyl carbonium ion, where the precursor of this carbonium ion is definitely the cyclic isomer^{15,16} (LVII) of O-benzoyl benzoic acid.

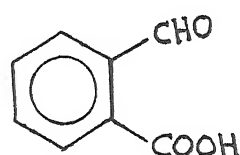


The formation of lactol intermediate has also been used to explain some of the other chemical reactions of O-benzoyl benzoic acid e.g. the reductive coupling¹⁷ of the acid with phosphorus and hydroiodic acid. The cyclic structure for pseudoesters has been confirmed by I.R.¹⁸ and Raman spectra¹⁹.

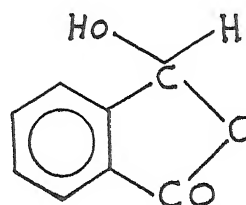
O-acetyl benzoic acid has been shown to yield an acetyl derivative through the formation of lactol⁹ intermediate as in the case of O-benzoyl benzoic acid. Peculiarly enough O-acetyl benzoyl chloride chemically behaves abnormally. All attempts fail to convert O-acetyl benzoyl chloride into O-acetyl benzaldehyde by a Rosenmund reduction or into O-diacetyl benzene²⁰. Its conversion to amides with amines has also resulted in failure or very poor yield²¹. This abnormal chemical behaviour of O-acetyl benzoyl chloride is actually to be expected, if one considers that acid chloride prepared in each case with thionyl chloride, is undoubtedly cyclic, and ring tautomeric acid chlorides invariably lead to cyclic products rather than those intended in the above preparative attempts. The lactol formation has been further confirmed by IR²² and NMR²³ spectral studies. Recently it has been reported that acid in liquid form, exists chiefly in lactol²⁴ form.

The formation of pseudoesters as well as large number of all other alkyl derivatives^{25,26} of phthal aldehydic acid(LXI) can be explained by considering the lactol (LXII) form of acid. NMR spectra of phthalaldehydic acid and O-acetyl benzoic acid

indicate that acids chiefly exist in cyclic forms²⁷. IR spectrum of phthal aldehydic acid shows bands at 3322 cm^{-1} , 1755 cm^{-1} and 1745 cm^{-1} which support the presence of acid chiefly in lactol form.

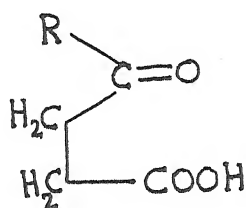


(LXI)

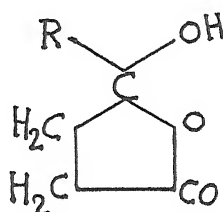


(LXII)

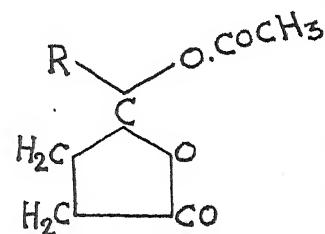
Openchain γ -keto acids i.e. Levulinic acid or β -acetyl propionic acid [(LXIII), $R=\text{CH}_3$] and β -benzoyl propionic acid [(LXIII), $R=\text{C}_6\text{H}_5$] have also been reported to exist in their tautomeric lactol forms (LXIV).



(LXIII)



(LXIV)



(LXV)

These two γ -keto acids form acetyl derivatives^{12,13} (LXV) which is possible through their lactol form only. Due to this type of chemical behaviour, the levulinic acid has been shown to be a mixture of ring and chain tautomers^{7,8}. It has

been noted that ring tautomerism²⁷ is further exalted by changing R to larger alkyl or aryl groups and it further increases when hydrogen atoms on α -carbon atom to carboxylic group, are also changed to larger alkyl group or α, β -ethylenic bond²⁸. Invariably the cyclic isomer has been found to predominate in solution.

I.R. STUDIES OF γ -KETO ACIDS AND THEIR ACETYL DERIVATIVES.

Fourteen γ -keto acids (on page) in four different series i.e. A,B,C and D have been used for the preparation of dyes described in the thesis. I.R. spectral examination of these acids clearly reveals their existence as a mixture of ring and chain tautomers. There are notable peaks showing the presence of diaryl ketonic $>C=O$ ($1635-1700\text{Cm}^{-1}$), aryl ketonic $-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{Ar}$ ($1660-1665\text{Cm}^{-1}$), Carboxyl $>C=O$ ($1695-1710\text{Cm}^{-1}$), Lactonic $>C=O$ ($1735-1755\text{Cm}^{-1}$), Carboxyl $-\text{OH}$ ($2600-2700\text{Cm}^{-1}$), Lactol $-\text{OH}$ ($3300-3660\text{Cm}^{-1}$) and phenolic $-\text{OH}$ ($3500-3600\text{Cm}^{-1}$).

I.R. spectra of the acetyl derivatives of the acids were also studied. It shows notable peaks of ~~carboxyl~~ $>C=O$ in acetate (new peaks $1000-1250$ and $1735-1760\text{Cm}^{-1}$) and lactonic $>C=O$ ($1735-1785\text{Cm}^{-1}$). The peaks, due to diaryl ketonic $>C=O$ ($1670-1700\text{Cm}^{-1}$), aryl ketonic $-\text{CH}_2-\text{CO}-\text{C}_6\text{H}_5$ ($1660-1675\text{Cm}^{-1}$), carboxyl $>C=O$ ($1695-1710\text{Cm}^{-1}$), carboxyl $-\text{OH}$ ($2600-2700\text{Cm}^{-1}$) and lactol $-\text{OH}$ ($3300-3660\text{Cm}^{-1}$), which were present originally in acids, were found absent in acetyl derivatives of the acids.

NMR STUDIES OF γ -KETO ACIDS AND THEIR DERIVATIVES:

Chemical shifts recorded in NMR spectra of different acids (1 to 14) and their derivatives further confirm the presence of lactol tautomer in each case (τ = 4.2-4.35) which disappears in the case of their acetyl derivatives and a new chemical shift of $-\text{OCOCH}_3$ (τ = 7.65-7.85) was observed. Thus it is amply clear that the γ -keto acids exist in keto as well as lactol form, which makes it possible to condense these acids with different phenolic compounds giving unsymmetrical phthaleins and succineins. In addition to the above characteristic chemical shifts others were mostly of aromatic protons (τ = 1.8-3.50) depending on the chemical environment in the aromatic rings. However, chemical shift of COOH in the keto form could not be recorded as NMR spectra were recorded on varian A-60. $-\text{NH}_2$ protons chemical shift has been observed at (τ = 6.45-6.65). The phenolic $-\text{OH}$ proton and the $-\text{COOCH}_3$ protons chemical shifts have been observed at about 4.80 τ and 5.90 τ respectively.

Acids & their Acetyl derivatives	Diaryl ketonic >C=O	Aryl ketonic -CH ₂ -C-Ar O	Carbo- nyl >C=O	Lacto- nic >C=O	Carboxyl -OH	Lactol -OH	Phenolic -OH	Ester group >C=O
1	2	3	4	5	6	7	8	9
(1) O-(4-amino 3-chloro benzoyl) benzoic acid. Acetyl derivative	1690	-	1710	1735	2665(Weak)	3660	-	-
	-	-	-	1785	-	-	-	1750, 1235, 1230, 1010.
(2) O-(3-carbomethoxy 4-hydroxy benzoyl)benzoic acid. Acetyl derivative.	1695	-	1705	1735	2665(Weak)	3660	3560	1730
	-	-	-	1780	-	-	-	1745, 1230, 1210, 1005.
(3) O-(2-hydroxy 5-methyl benzoyl) benzoic acid. Acetyl derivative	1670	-	1710	1735	2700(Weak)	3500	3600	-
	-	-	-	1785	-	-	-	1750, 1245, 1205, 1010.
(4) O-(3,4-dimethyl benzoyl)benzoic acid. Acetyl derivative.	1690	-	1710	1740	2640(Weak)	3640	-	-
	-	-	-	1795	-	-	-	1760, 1240, 1220, 1015.

Acids & their Acetyl derivatives	Diaryl ketonic >C=O	Aryl ketonic -CH ₂ -C(=O)-Ar	Carbo- nyl >C=O	Lacto- nic >C=O	Carboxyl -OH	Lactol -OH	Phenolic -OH	Ester group >C=O
1	2	3	4	5	6	7	8	9
(1) O-(4-amino 3-chloro benzoyl) benzoic acid. Acetyl derivative	1690	-	1710	1735	2665 (Weak)	3660	-	-
(2) O-(3-carbomethoxy 4-hydroxy benzoyl) benzoic acid. Acetyl derivative.	1695	-	1705	1735	2665 (Weak)	3660	3560	1730
	-	-	-	1780	-	-	-	1745, 1230, 1210, 1005.
(3) O-(2-hydroxy 5-methyl benzoyl) benzoic acid. Acetyl derivative	1670	-	1710	1735	2700 (Weak)	3500	3690	1750, 1245, 1205, 1010.
	-	-	-	1785	-	-	-	-
(4) O-(3,4-dimethyl benzoyl) benzoic acid. Acetyl derivative.	1690	-	1710	1740	2640 (Weak)	3640	-	-
	-	-	-	1785	-	-	-	1760, 1240, 1220, 1015.

	1	2	3	4	5	6	7	8	9
(5) O-(4-amino									
3-chloro benzoyl)					1742	2655(Weak)	3300	-	-
tetra chloro		1700	-	1705					
benzoic acid.					1785	-	-	-	1760, 1250, 1230, 1010.
Acetyl		-	-	-					
derivative.									

(6) O-(3-carbomethoxy									
4-hydroxy benzo-					1745	2640(Weak)	3500	3620	1730
yl) tetra chloro		1690	-	1705					
benzoic acid.					1785	-	-		1760, 1250, 1230, 1010.
Acetyl		-	-	-					
derivative.									

(7) O-(2-hydroxy									
5-methyl benzoyl)					1755	2600(Weak)	3500	3600	-
tetra chloro		1678	-	1705					
benzoic acid.					1785	-	-	-	1745, 1235, 1210, 1005.
Acetyl		-	-	-					
derivative.									

(8) O-(3,4-dimethyl									
benzoyl) tetra					1740	2620(Weak)	3550	-	-
chloro benzoic		1685	-	1700					
acid.									1755, 1240, 1210, 1005.
Acetyl		-	-	-	1785	-	-	-	
derivative.									

1	2	3	4	5	6	7	8	9
(9) O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid.	1662	-	1695	1745	2650	3300	-	-
Acetyl derivative.	-	-	-	1785	-	-	-	1750, 1250, 1220, 1030.
(10) O-(2-hydroxy 5-methyl benzo- yl) m-nitro benzoic acid.	1675	-	1705	1755	2660 (Weak)	3500	3600	-
Acetyl derivative.	-	-	-	1785	-	-	-	1745, 1240, 1210, 1005.
(11) O-(3,4-dimethyl benzoyl)m-nitro benzoic acid.	1680	-	1700	1750	2680 (Weak)	3485	-	-
Acetyl derivative.	-	-	-	1785	-	-	-	1740, 1250, 1210, 1020.
(12) β -(4-amino 3-chloro benzoyl) propionic acid.	1695	1665	1710	1742	2640 (Weak)	3500	-	-
Acetyl derivative.	-	-	-	1778	-	-	-	1745, 1230, 1205, 1000.

(13) β -(2-hydroxy

5-methyl

benzoyl)

propionic

acid.

Acetyl

derivative.

1638

1660

1705

1735

2620(Weak)

3460

3580

-

1740, 1240,
1210, 1005.

(14) β -(3,4-dimethyl

benzoyl)

propionic

acid.

Acetyl

derivative.

1680

1660

1705

1740

2610(Weak)

3490

-

-

1745, 1240,
1210, 1010.

NMR SPECTRA OF α -KETO ACIDS AND THEIR ACETYL DERIVATIVES

Acids and their acetyl derivatives.	Solvent	Chemical shift (τ)
1	2	3
(1) O-(4-amino 3-chloro benzoyl) benzoic acid.	CDCl ₃	1.90-3.45(m; 7 unsymmetrical aromatic protons); 4.30(br; S; lactol proton); 6.65(S; 2-NH ₂ protons).
Acetyl derivative.	CDCl ₃	1.90-3.40(m; 7 unsymmetrical aromatic protons); 7.62(S; 3-OOCCH ₃ protons); 3.2(br; S; 1-NH-COCH ₃ proton) 7.92(S; 3-NH-COCH ₃ protons).
(2) O-(3-carbomethoxy 4-hydroxy benzoyl) benzoic acid.	CDCl ₃	1.85-3.40(m; 7 unsymmetrical aromatic protons); 4.32(br; S; lactol proton); 4.78(S; 1 phenolic -OH proton); 5.90(S; 3-COOCH ₃ protons).
Acetyl derivative.	CDCl ₃	1.80-3.35(m; 7 unsymmetrical aromatic protons); 7.65(S; 3 lactol -OOCCH ₃ protons); 7.80(S; phenolic 3-OOCCH ₃ protons); 5.90(S; 3-COOCH ₃ protons).
(3) O-(2-hydroxy 5-methyl benzoyl) benzoic acid.	DMSO	1.90-3.05(m; 7 unsymmetrical ring protons); 4.30(br; S; lactol proton); 7.85(S; 3-CH ₃ protons); 4.8 (S; 1 phenolic -OH proton).
Acetyl derivative.	CDCl ₃	1.80-2.90(m-7 unsymmetrical aromatic protons); 7.60(S; lactol 3-OOCCH ₃ protons); 7.85(S; 3-CH ₃ protons) 7.8 (S; phenolic 3-OOCCH ₃ protons).
(4) O-(3,4-dimethyl benzoyl) benzoic acid.	DMSO	1.90-3.45(m; 7 unsymmetrical aromatic protons); 4.32 (br; S; lactol proton); 7.85 (S; 6 two-CH ₃ protons).
Acetyl derivative.	CDCl ₃	1.88-3.42(m; 7 unsymmetrical aromatic protons); 7.90(S; 6 two-CH ₃ protons); 7.60(S; lactol 3-OOCCH ₃ protons).

1	2	3
(5) O-(4-amino 3-chloro benzoyl) tetra chloro benzoic acid. Acetyl derivative.	DMSO CDCl ₃	2.05-3.25(m; 3 unsymmetrical aromatic protons); 4.32(br;S; lactol 1-OH proton); 6.60(S; 2-NH ₂ protons). 2.20-3.45(m; 3 unsymmetrical aromatic protons); 7.76(S; 3-O.OCH ₃ protons); 7.85(S; 3-NH-COCH ₃ protons); 3.20(br;S; 1-NH-COCH ₃ proton).
(6) O-(3-carbomethoxy 4-hydroxy benzoyl) tetra chloro benzoic acid. Acetyl derivative.	DMSO CDCl ₃	2.30-3.20(m; 3 unsymmetrical aromatic protons); 4.30(S;br; lactol 1-OH proton); 4.78(S; 1 phenolic OH proton); 5.90(S; 3-COOCH ₃ protons). 2.35-3.40(m; 3 unsymmetrical aromatic protons); 7.60(S; lactol 3-O.OCH ₃ protons); 5.90(S; 3-COOCH ₃ protons); 7.80(S;phenolic 3-OOCCH ₃ protons).
(7) O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid. Acetyl derivative.	DMSO CDCl ₃	1.85-3.90(m; 3 unsymmetrical aromatic protons); 4.30(br;S; lactol -OH proton); 7.82(S; 3-CH ₃ protons); 4.8 (S; 1 phenolic -OH proton). 1.95-3.05(m; 3 unsymmetrical aromatic protons); 7.8 (S; 3 phenolic -O.OCH ₃ protons); 7.90(S; 3-CH ₃ protons); 7.60(S; 3 lactol -O.OCH ₃ protons).
(8) O-(3,4-dimethyl benzoyl) tetra chloro benzoic acid. Acetyl derivative.	DMSO CDCl ₃	2.30-3.25(m; 3 unsymmetrical protons); 4.32(br;S; lactol 1-OH proton); 7.90(S; 6 two CH ₃ protons). 2.35-3.20(m; 3 unsymmetrical aromatic protons); 7.60(S; lactol 3-O.OCH ₃ protons); 7.82(S; 6 two-CH ₃ protons).
(9) O-(4-amino 3-chloro benzoyl) p-nitro benzoic acid. Acetyl derivative.	DMSO CDCl ₃	2.30-3.32(m; 6 unsymmetrical ring protons); 4.30(br;S; lactol -OH proton); 6.62(S; 2-NH ₂ protons). 2.32-3.45(m; 6 unsymmetrical aromatic protons); 7.60(S; 3-O.OCH ₃ protons); 3.20(br;S; 1-NH-COCH ₃ proton); 7.90(S; 3-NH-CO-CH ₃ protons).

(10) O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid.	DMSO	2.05-2.95(m; 6 unsymmetrical ring protons); 4.30(br;s; lactol -OH proton); 7.85(s; 3-CH ₃ protons); 4.8 (s; 1 phenolic -OH proton).
Acetyl derivative.	CDCl ₃	2.05-3.45(m; 6 unsymmetrical aromatic protons); 7.60(s; 3 lactol -O.OCC ₃ protons); 7.90(s; 3-CH ₃ protons) 7.80(s; 3-phenolic-O.OCC ₃ protons).
(11) O-(3,4-dimethyl benzoyl) m-nitro benzoic acid.	DMSO	2.35-3.25(m; 6 unsymmetrical protons); 4.32(br;s;lactol -OH proton); 7.90(s; 6 two-CH ₃ protons).
Acetyl derivative.	CDCl ₃	2.05-3.15(m; 6 unsymmetrical aromatic protons); 7.62(s; 3-O.OCC ₃ protons); 7.80(s; 6 two-CH ₃ protons).
(12) β-(4-amino 3-chloro benzoyl) propionic acid.	DMSO	2.20-3.45(m; 3 unsymmetrical aromatic protons); 6.65(s; 2-NH ₂ protons); 4.25(br;s; lactol -OH proton); 9.5 (triplet; 2-CH ₂ ring protons); 8.65(triplet; 2-CO-CH ₂ ring protons).
Acetyl derivative.	CDCl ₃	2.10-3.45(m; 3 unsymmetrical aromatic protons); 3.25(br;s; 1-NH-COCH ₃ proton); 7.80(s; 3-NH-COCH ₃ protons) 7.60(s;lactol 3-O.OCC ₃ protons); 9.65(triplet 2-CH ₂ ring protons); 8.58(triplet; 2-CO-CH ₂ ring protons).
(13) β-(2-hydroxy 5-methyl benzoyl) propionic acid.	DMSO	2.05-3.00(m; 3 unsymmetrical ring protons); 4.30(br;s; lactol -OH proton); 7.85(s; 3-CH ₃ protons); 4.82(s; 1-phenolic -OH proton); 9.5(triplet 2-CH ₂ ring protons); 8.65(triplet, 2-CO-CH ₂ ring protons).
Acetyl derivative.	CDCl ₃	2.10-3.45(m; 3 unsymmetrical protons); 7.60(s;lactol 3-O.OCC ₃ protons); 7.95(s; 3-CH ₃ protons); 9.65(triplet 2-CH ₂ ring protons); 8.60(triplet, 2-CO-CH ₂ ring protons); 7.80(s;phenolic 3-O.OCC ₃ protons).

1																	
2																	
3																	

(14) β -(3,4-dimethyl benzoyl) propionic acid.

Acetyl derivative.

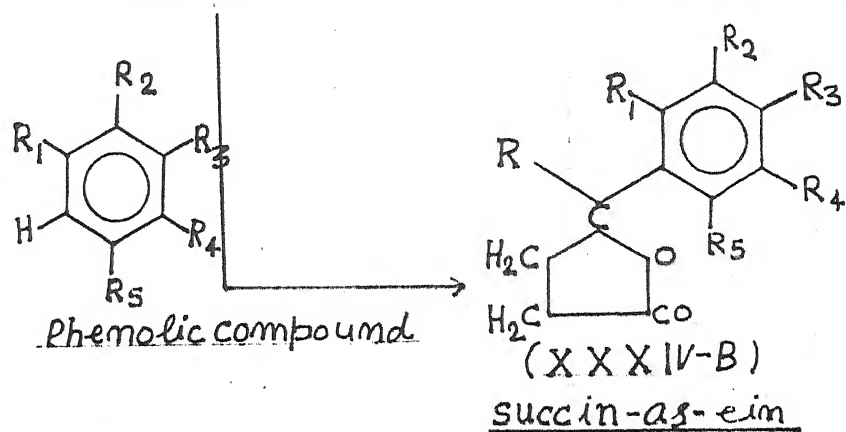
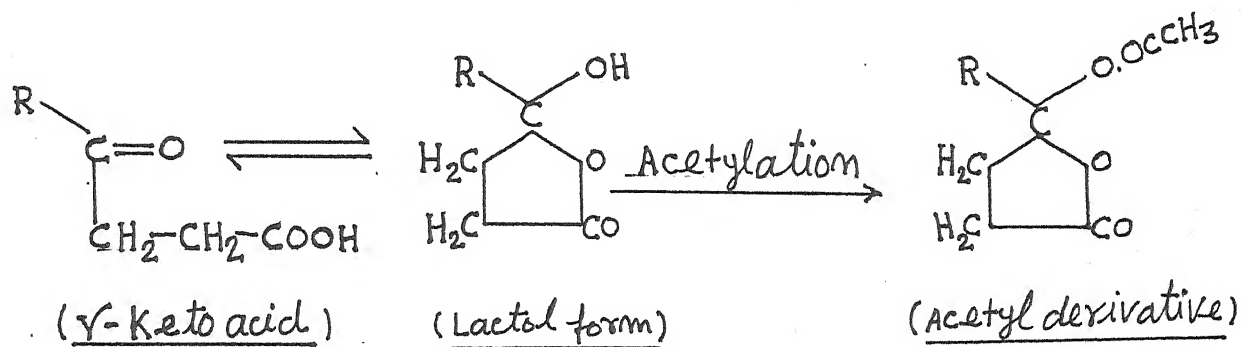
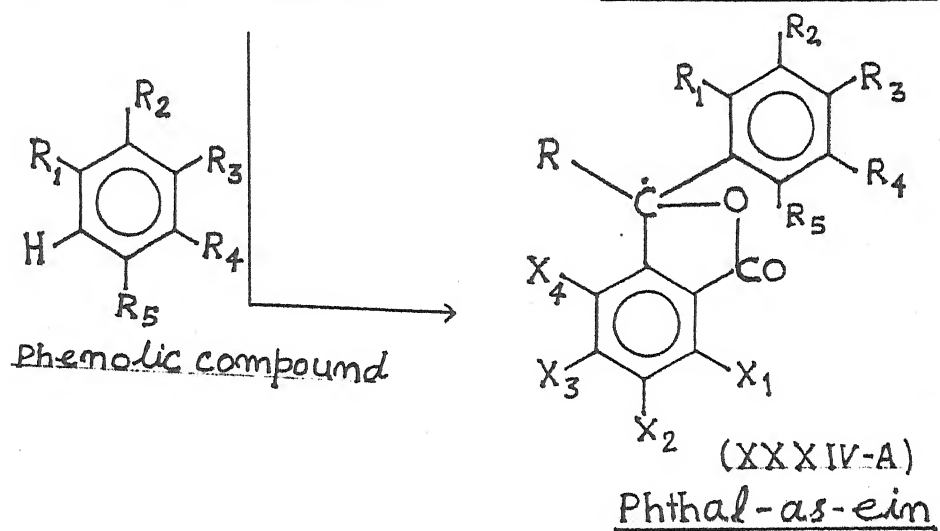
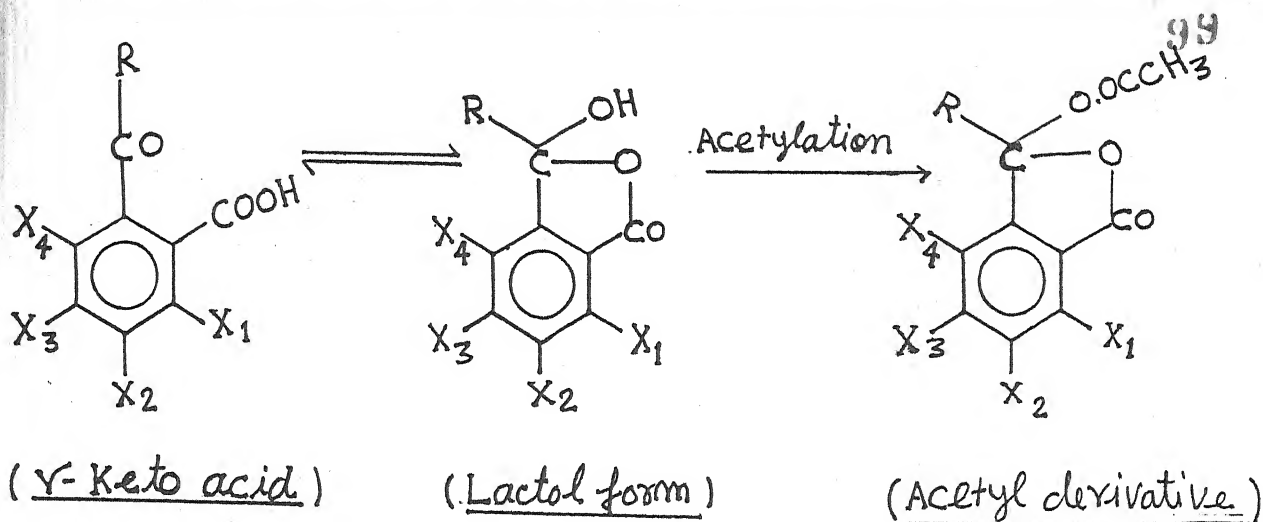
CDCl₃

1.90-3.05(m; 3 unsymmetrical ring protons);
4.30(br;s;lactol proton); 7.90(S; 6 two-CH₃ protons);
9.65(triplet; 2-CH₂ ring protons); 8.62(triplet; 2-CO-CH₂ ring protons).

2.15-3.05(m; 3 unsymmetrical aromatic protons);
7.65(S;lactol 3-O-OCCH₃ protons); 9.62(triplet; 2-CH₂ ring protons); 8.60 triplet; 2-COCH₂ ring protons).

Thus from the IR and NMR spectral studies of acids and their acetyl derivatives, it is quite clear that γ -keto acids exhibit the phenomenon of ring chain tautomerism and most of their chemical reactions take place via more stable lactol (ring) form. Now it is quite definite that cyclisation of γ -keto acids provides a hydroxyl group in the form of the corresponding lactol, which is capable of condensing with various aromatic hydroxy compounds resulting in the formation of novel analogues of phthalein, (phthal-as-eins) and succineins (succin-as-eins). It is also quite reasonable to conclude that acetylation of γ -keto acids takes place via ring tautomer (lactol form), and also that the acetyl derivatives of the acids, phthal-as-eins and succin-as-eins possess cyclic structure.

Thus the formation of acetyl derivatives of phthal-as-eins and succin-as-eins from various γ -keto acids may be shown in following general structure.



Recently Gupta et.al.²⁹⁻⁴⁵ and Beg and Coworkers⁴⁶⁻⁴⁷ have reported the preparation of large number of mixed phthaleins and succineins from γ -keto acids. They have also shown that lactol form of γ -keto acids is involved in the synthesis of these compounds.

PART - BCHEMICAL STRUCTURE OF PHTHAL-AS-EIN AND SUCCIN-AS-EIN DYES

Here an attempt has been made to assign suitable and satisfactory chemical structures to various novel analogues of phthaleins (phthal-as-eins) and succineins (succin-as-eins), (incorporated in the thesis) on the basis of their chemical behaviour and study of IR and NMR spectra of α -keto acids (used for synthesis of phthal-as-eins and succin-as-eins) and their corresponding acetyl derivatives. To establish the chemical structure, following fourteen representative dyes have been chosen.

- 1.A. (4-amino 3-chloro phenyl) resorcinol phthal-as-ein.
B. (4-amino 3-chloro phenyl) resorcinol tetra chloro phthal-as-ein.
C. (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein.
- 2.A. (3-carbomethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein.
B. (3-carbomethoxy 4-hydroxy phenyl) resorcinol tetra chloro phthal-as-ein.
- 3.A. (2-hydroxy 5-methyl phenyl) resorcinol phthal-as-ein.
B. (2-hydroxy 5-methyl phenyl) resorcinol tetra chloro phthal-as-ein.
C. (2-hydroxy 5-methyl phenyl) resorcinol nitro phthal-as-ein.
- 4.A. (3,4-dimethyl phenyl) resorcinol phthal-as-ein.
B. (3,4-dimethyl phenyl) resorcinol tetra chloro phthal-as-ein.
C. (3,4-dimethyl phenyl) resorcinol nitro phthal-as-ein.

- 5.A. (4-amino 3-chloro phenyl) resorcinol succin-as-ein.
B. (2-hydroxy 5-methyl phenyl) resorcinol succin-as-ein.
C. (3,4-dimethyl phenyl) resorcinol succin-as-ein.

For each dye a suitable molecular structure has been suggested on the basis of its elemental analysis, molecular weight determination, identification and determination of the number of characteristic functional groups. Study of brominated product and determination of number of bromine atoms in each case has been used to determine the number of resorcinol molecules in a dye. Each dye has also been subjected to caustic potash treatment which helped in assigning the structure to the dye on more firm basis.

The structure of the dyes chosen have been further supported by IR spectra of the dyes and their acetyl derivatives. Each dye shows peaks due to lactonic $>C=O$ ($1735-1785\text{ cm}^{-1}$) and phenolic hydroxyl group ($3300-3600\text{ cm}^{-1}$). The peak due to hydroxyl group does not appear in the IR spectra of acetyl derivatives. New ester peaks have been observed in the range of $1000-1255\text{ cm}^{-1}$ in the IR spectra of the acetyl derivatives.

STRUCTURE OF :

- 1.(A) (4-AMINO 3-CHLORO PHENYL) RESORCINOL PHTHAL-AS-EIN.
- (B) (4-AMINO 3-CHLORO PHENYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN.
- (C) (4-AMINO 3-CHLORO PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN.

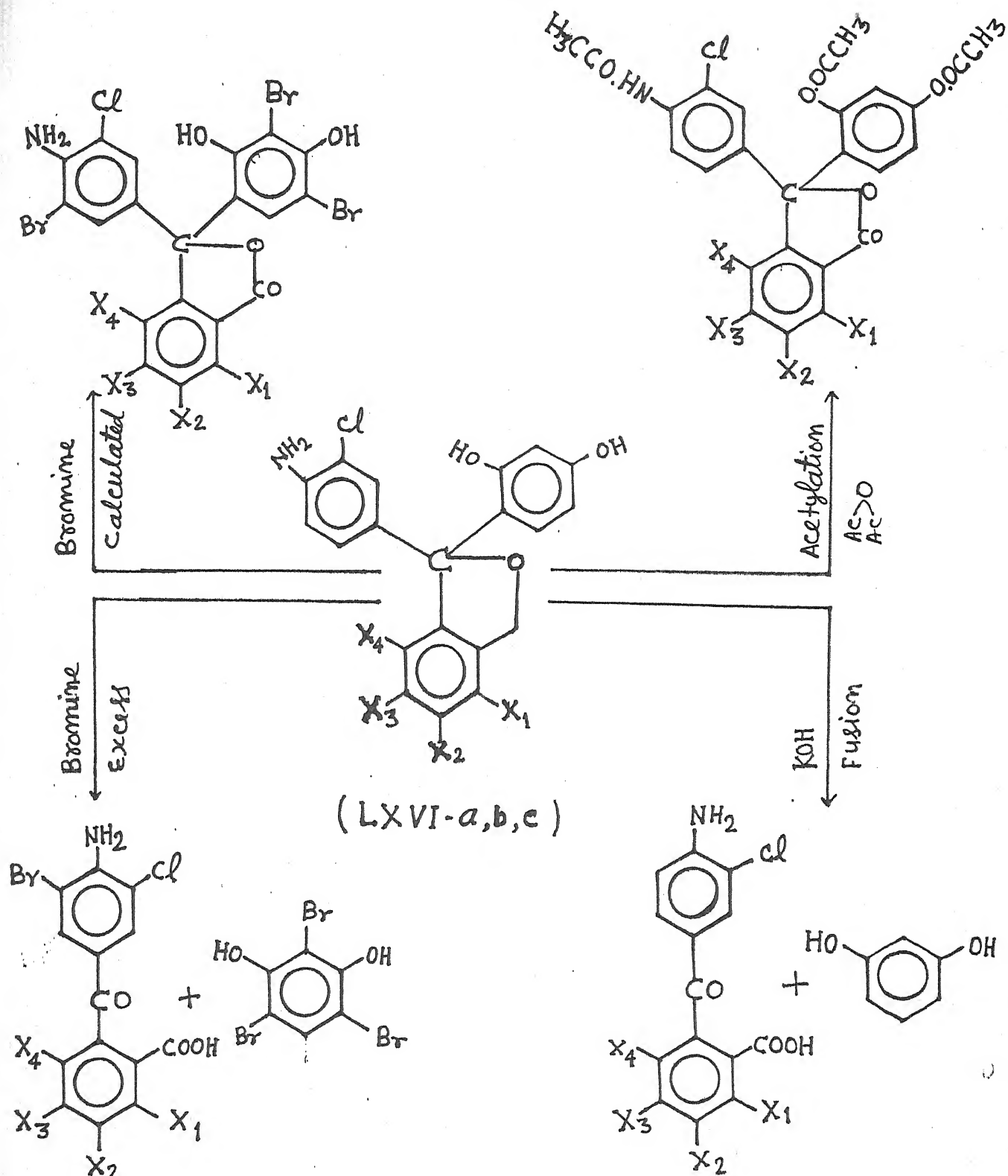
1.(A) The dye prepared by condensing O-(4-amino 3-chloro benzoyl) benzoic acid and resorcinol in presence of 3,4-drops of concentrated sulphuric acid as the condensing agent (page 132). The dye thus produced has molecular formula $C_{20}H_{14}NClO_4$, molecular weight 367.5. When acetylated the dye yielded a tri acetyl derivative, indicating the presence of two phenolic and an amino group. On bromination with calculated amount of bromine it yielded a tri bromo derivative showing the presence of only a molecule of resorcinol in the dye molecule. One bromine atom is substituted in the ring containing amino group. When fused with caustic potash the dye yielded O-(4-amino 3-chloro benzoyl) benzoic acid alongwith a molecule of resorcinol. With excess of bromine the dye gave tribromo resorcinol and a mono bromo derivative of O-(4-amino 3-chloro benzoyl) benzoic acid. Based on these chemical evidences the structure (LXVI-a) has been assigned to the dye molecule.

1.(B) The acid O-(4-amino 3-chloro benzoyl) tetra chloro benzoic acid, when condensed with resorcinol in presence of few drops of concentrated sulphuric acid, yielded (4-amino 3-chloro phenyl) tetra chloro phthal-as-ein. The dye thus produced (Mol.for. $C_{20}H_{10}NCl_5O_4$, Mol.wt. 505.5) on acetylation

gave a triacetyl derivative and a tri bromo derivative when brominated with calculated amount of bromine. Formation of a tri acetyl and tri bromo derivative of the dye clearly indicates the presence of only one resorcinol unit in the dye molecule. Caustic potash fusion of the dye gave a molecule of O-(4-amino 3-chloro benzoyl) tetra chloro benzoic acid alongwith a molecule of resorcinol. Treatment of the dye with excess of bromine gave mono bromo derivative of the same acid alongwith a molecule of tri bromo resorcinol. All these reactions have been explained by assigning the structure (LXVI-b) of the dye.

1.(C) The dye (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein having molecular formula $C_{20}H_{13}N_2ClO_6$, Mol.wt. 412.5, was prepared by condensing O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid with resorcinol in presence of few drops of conc. sulphuric acid (page 207). The dye yielded tri acetyl derivative and tri bromo derivative on acetylation and bromination with calculated amount of bromine respectively. Thus showing the presence of only one resorcinol unit in the dye molecule and an amino group in the dye molecule. Caustic potash fusion of the dye yielded O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid alongwith a molecule of resorcinol. Treatment of the dye with excess of bromine yielded a mono bromo derivative of the same acid and a molecule of tri bromo resorcinol. All the above reactions may be explained by assigning the structure (LXVI-c) of the dye molecule.

All the reactions of the dyes (LXVI-a, LXVI-b, and LXVI-c) are shown in chart - A, page 105 .



LXVI-a $X_1 = X_2 = X_3 = X_4 = H$

LXVI-b $X_1 = X_2 = X_3 = X_4 = Cl$

LXVI-c $X_1 = X_2 = X_3 = H; X_4 = NO_2$

STRUCTURE OF :

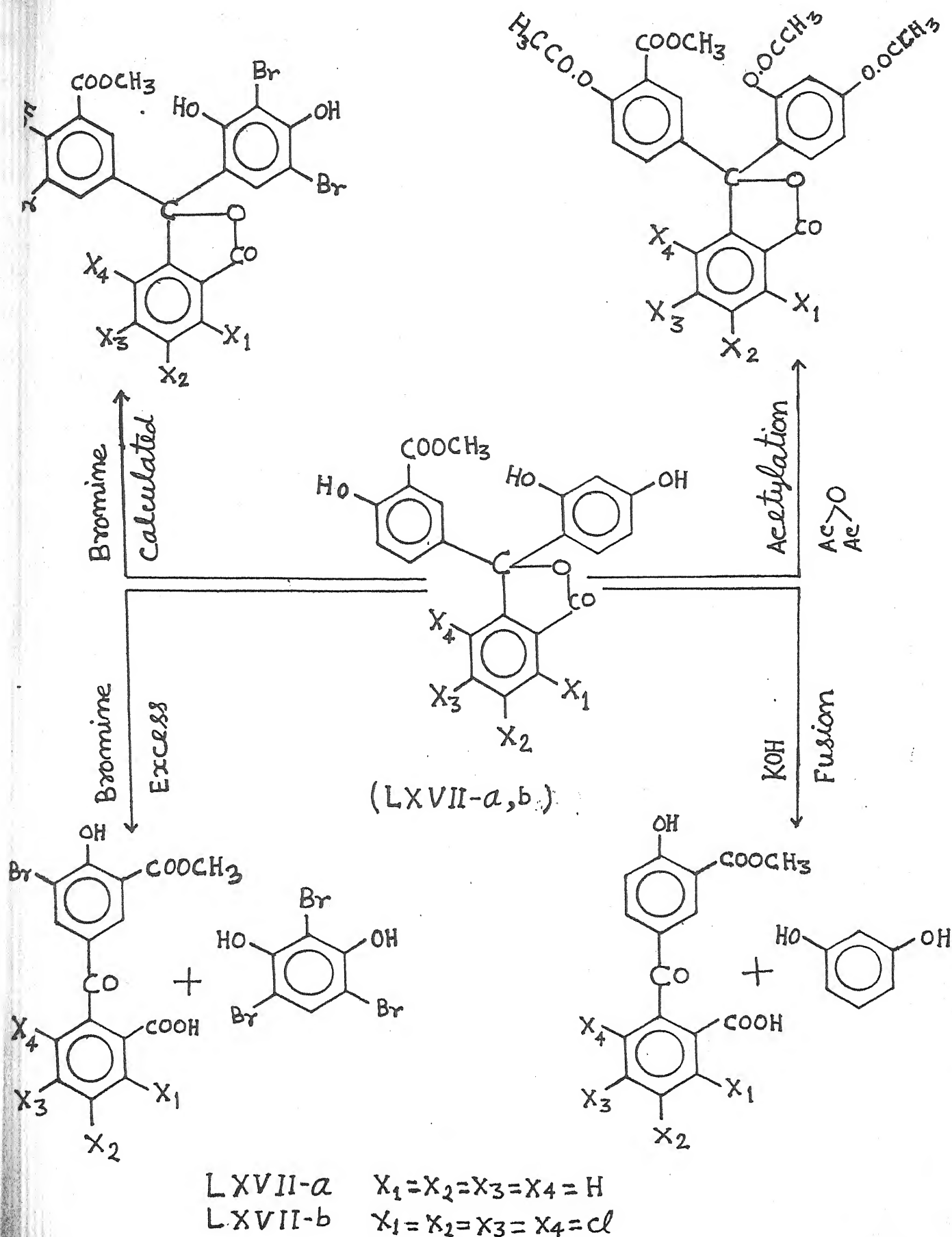
- 1.(A) (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL PHTHAL-AS-EIN.
 (B) (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN.

1.(A) The dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein having molecular formula $C_{22}H_{16}O_7$, molecular weight 392.0 was prepared by condensing O-(3-carbmethoxy 4-hydroxy benzoyl) benzoic acid with resorcinol in presence of conc. sulphuric acid as the condensing agent. The dye on acetylation formed a tri acetyl derivative and on bromination yielded a tri bromo derivative indicating the presence ^{of} in all three phenolic groups in the dye molecule. Thus only one resorcinol molecule is present in the dye molecule. The dye when treated with excess of bromine yielded mono bromo derivative of the acid and a molecule of tri bromo resorcinol. Caustic potash fusion of the dye yielded the acid O-(3-carbmethoxy 4-hydroxy benzoyl) benzoic acid alongwith a molecule of resorcinol. Based on these chemical evidences the dye molecule has been assigned the structure (LXVII.a).

2.(B) The acid O-(3-carbmethoxy 4-hydroxy benzoyl) tetra chloro benzoic acid when condensed with resorcinol in presence of few drops of conc. sulphuric acid as the condensing agent, yielded the dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol tetra chloro phthal-as-ein, mol.for. $C_{22}H_{12}Cl_4O_7$, mol.wt. 530.0. It on acetylation and bromination (with calculated

amount of bromine) yielded tri acetyl and tri bromo derivatives of the dye showing the presence of in all three phenolic groups in the dye molecule. Treatment of the dye with excess of bromine yielded a mono bromo derivative of the acid taken for condensation alongwith a ^{molecule of} tri bromo resorcinol. Caustic potash fusion of the dye yielded O-(3-carbmethoxy 4-hydroxy benzoyl) tetra chloro benzoic acid, alongwith a molecule of resorcinol. All these reactions have been explained by assigning the structure (LXVII-b) of the dye molecule.

All the reactions of the dyes (LXVII-a and LXVII-b) are shown in chart B. (Page 108).



STRUCTURE OF :

- 3.(A) (2-HYDROXY 5-METHYL PHENYL) RESORCINOL PHTHAL-AS-EIN.
 (B) (2-HYDROXY 5-METHYL PHENYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN.
 (C) (2-HYDROXY 5-METHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN.

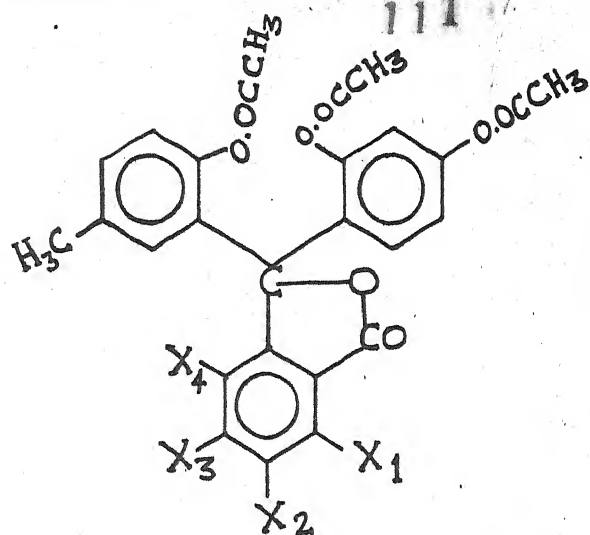
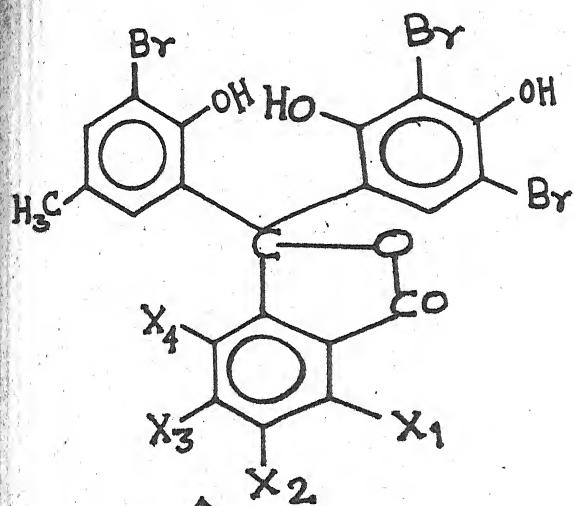
3.(A) The acid O-(2-hydroxy 5-methyl benzoyl) benzoic acid when condensed with resorcinol in presence of 3-4 drops of conc.sulphuric acid, as the condensing agent (page 151) yielded the dye (2-hydroxy 5-methyl phenyl) resorcinol phthal-as-ein, mol.for. $C_{21}H_{16}O_5$, mol.wt. 348.0. It on acetylation and bromination (with calculated amount of bromine) yielded tri acetyl and tri bromo derivatives of the dye, showing the presence of three phenolic groups in the dye molecule. Treatment of the dye with excess of bromine yielded a mono bromo derivative of O-(2-hydroxy 5-methyl benzoyl) benzoic acid alongwith a tri bromo derivative of resorcinol. Caustic potash fusion of the dye yielded same acid as mentioned above alongwith a molecule of resorcinol. All these reactions have been explained by assigning the structure (LXVIII-a) of the dye.

3.(B) The dye (2-hydroxy 5-methyl phenyl) resorcinol tetra chloro phthal-as-ein having molecular formula $C_{21}H_{12}O_5Cl_4$, Mol.wt. 486.0, was prepared by condensing O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid with resorcinol in presence of few drops of conc.sulphuric acid as the condensing agent (page 190). The dye on acetylation formed a tri acetyl derivative

and on bromination yielded a tri bromo derivative showing the presence of three phenolic groups in the dye molecule. Thus only one resorcinol molecule is present in the dye molecule. The dye when treated with excess of bromine yielded a mono bromo derivative of the O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid and a molecule of tri bromo resorcinol. Caustic potash fusion of the dye yielded the acid mentioned above, alongwith a molecule of resorcinol. Based on these chemical evidences the dye molecule has been assigned the structure (LXVIII-b).

3.(C) The dye prepared by condensing O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid and resorcinol in presence of 5-6 drops of conc.sulphuric acid as the condensing agent (page 217). The dye thus produced has molecular formula $C_{21}H_{15}NO_7$, mol.wt. 393.0. On acetylation gave a tri acetyl derivative and a tri bromo derivative when brominated with calculated amount of bromine. Formation of a tri acetyl and tri bromo derivative of the dye clearly indicates the presence of only one resorcinol unit in the dye molecule. Caustic potash fusion of the dye gave a molecule of O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid alongwith a molecule of resorcinol. Treatment of the dye with excess of bromine gave mono bromo derivative of the same acid alongwith a molecule of tri bromo resorcinol. On the basis of above chemical evidences the dye was assigned the structure (LXVIII-c).

The foregoing reactions of the dye (LXVIII-a, LXVIII-b and LXVIII-c) are shown in chart C (page 111).



Bromine
calculated

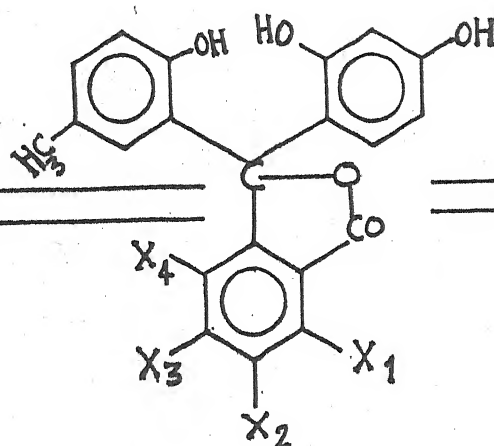
Acetylation

AC > 0
AC

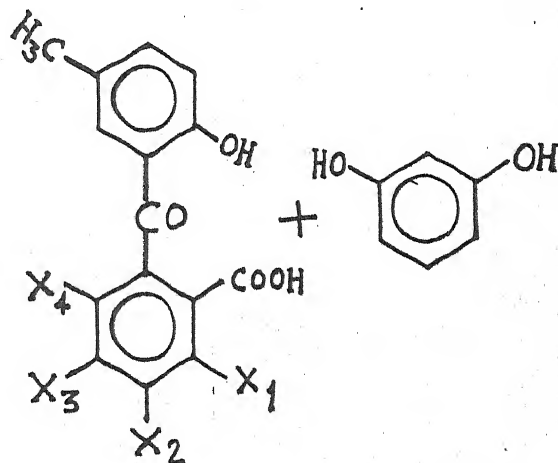
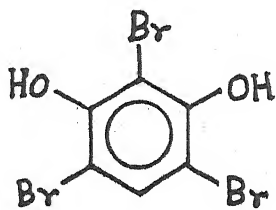
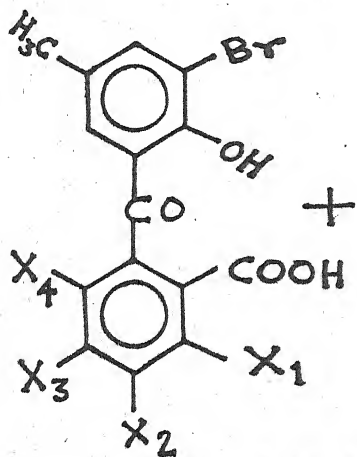
Bromine
Excess

KOH

Fusion



(LXVIII-a, b, c)



LXVIII-a $X_1=X_2=X_3=X_4=H$

LXVIII-b $X_1=X_2=X_3=X_4=Cl$

LXVIII-c $X_1=X_2=X_3=H; X_4=NO_2$

STRUCTURE OF :

- 4.(A) (3,4-DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN.
 (B) (3,4-DIMETHYL PHENYL) RESORCINOL TETRA CHLORO PHTHAL-
 -AS-EIN.
 (C) (3,4-DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN.

4.(A) The dye (3,4-dimethyl phenyl) resorcinol phthal-as-ein having molecular formula $C_{22}H_{18}O_4$, Mol.wt.346.0 was prepared by condensing O-(3,4-dimethyl benzoyl) benzoic acid with resorcinol in presence of few drops of conc.sulphuric acid as the condensing agent (page 160). The dye on acetylation yielded diacetyl derivative and on bromination with calculated amount of bromine, yielded dibromo derivative, thus indicating the presence of only a molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye gave a molecule of O-(3,4-dimethyl benzoyl benzoic acid and a molecule of resorcinol. The dye on treatment with excess of bromine yielded the same acid alongwith a molecule of tribromo resorcinol. Based on these chemical evidences the dye was assigned the structure(LXIX-a).

tetra chloro

4.(B) The acid O-(3,4-dimethyl benzoyl) benzoic acid when condensed with resorcinol in presence of 3-5 drops of conc. sulphuric acid as the condensing agent (page 198), yielded the dye (3,4-dimethyl phenyl) tetra chloro phthal-as-ein, having molecular formula $C_{22}H_{14}Cl_4O_4$, Mol.wt. 484.0. It on acetylation and bromination (with calculated amount of bromine) yielded diacetyl and dibromo derivative of the dye, showing the presence of one resorcinol unit in the dye molecule. Treatment of the dye

with excess of bromine yielded O-(3,4-dimethyl benzoyl) tetra chloro benzoic acid alongwith a molecule of tri bromo resorcinol. Caustic potash fusion of the dye yielded the acid, mentioned above, alongwith a molecule of resorcinol. All these reactions have been explained by assigning the structure (LXIX-b) of the dye molecule.

4.(C) The dye (3,4-dimethyl phenyl) resorcinol nitro phthal-as-ein was prepared by condensing O-(3,4-dimethyl benzoyl) m-nitro benzoic acid with resorcinol in presence of few drops of conc.sulphuric acid as the condensing agent (page 226). The dye having molecular formula $C_{22}H_{17}NO_6$, Mol.wt.391.0 gave diacetyl and dibromo derivatives on acetylation and bromination (with calculated amount of bromine) respectively. Thus only one molecule of resorcinol is present in the dye molecule. Caustic potash fusion of the dye yielded O-(3,4-dimethyl benzoyl) m-nitro benzoic acid and a molecule of resorcinol. The dye on treatment with excess of bromine yielded the same acid and a molecule of tri bromo resorcinol. On the basis of above chemical evidences the dye was assigned the structure (LXIX-c).

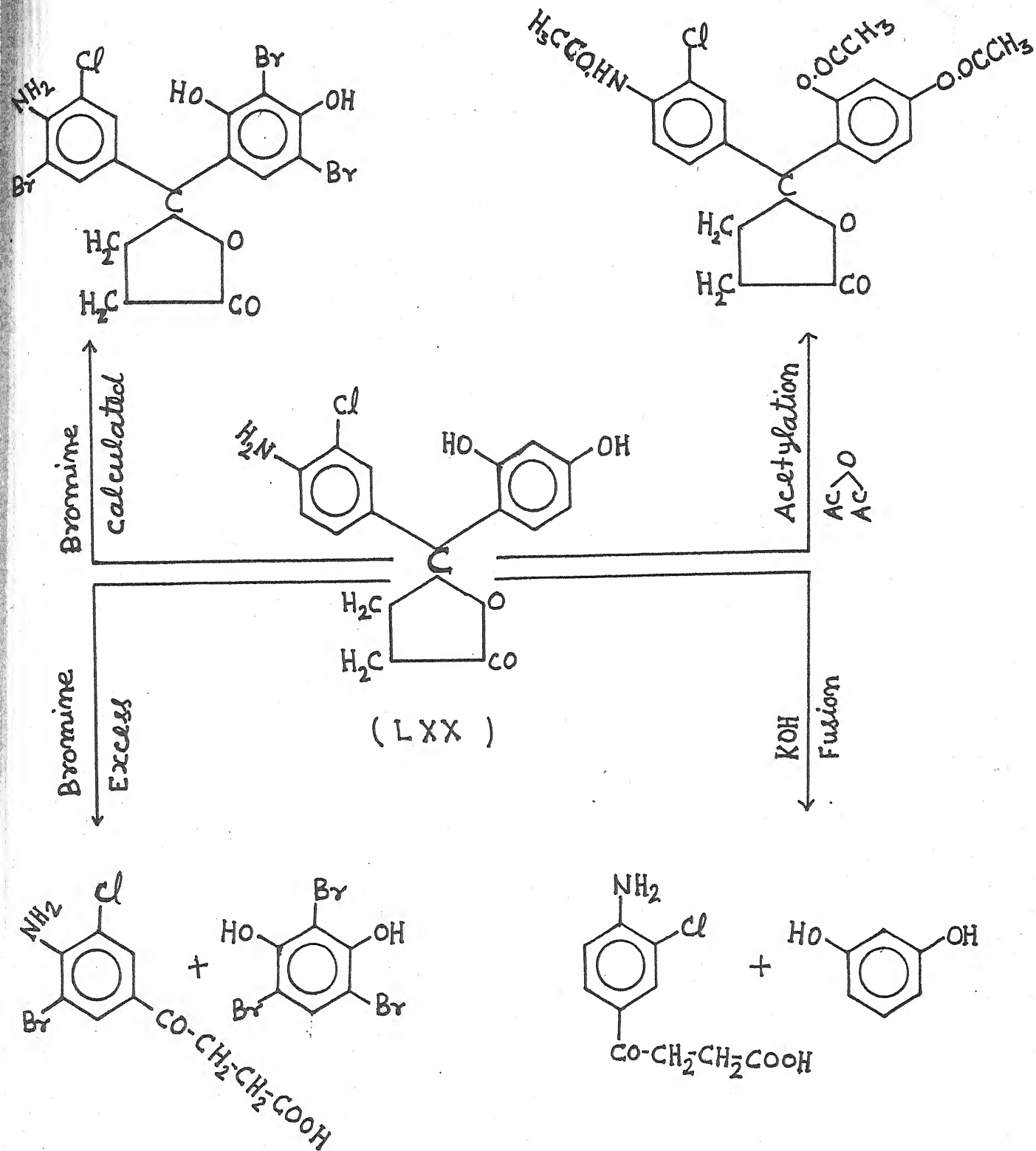
All the chemical reactions of the dyes (LXIX-a , LXIX-b and LXIX-c) are shown in chart D (page 114).

STRUCTURE OF :

5.(A) (4-AMINO 3-CHLORO PHENYL) RESORCINOL SUCCIN-AS-EIN.

The dye (4-amino 3-chloro phenyl) resorcinol succin-as-ein (Mol.for. $C_{22}H_{18}O_4$, Mol.wt. 346.0), was prepared by condensing the acid β -(4-amino 3-chloro benzoyl) propionic acid with resorcinol in presence of conc.sulphuric acid as the condensing agent (page 236). It on acetylation and bromination yielded triacetyl and tribromo derivatives respectively indicating the presence of only one resorcinol unit in the dye molecule. When treated with excess of bromine the dye yielded β -(3-bromo 4-amino 5-chloro benzoyl) propionic acid alongwith a tribromo resorcinol. Caustic potash fusion of the dye gave β -(4-amino 3-chloro benzoyl) propionic acid alongwith a molecule of resorcinol. All these reactions may be explained by assigning the structure (LXX) of the dye molecule.

All the above reactions are shown in chart E (page 116).

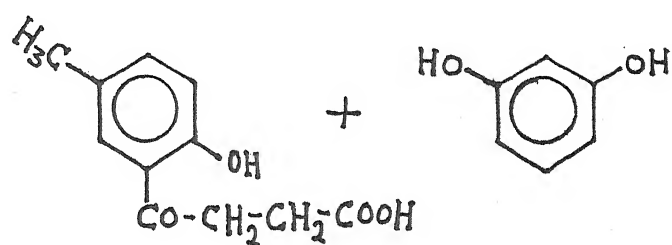
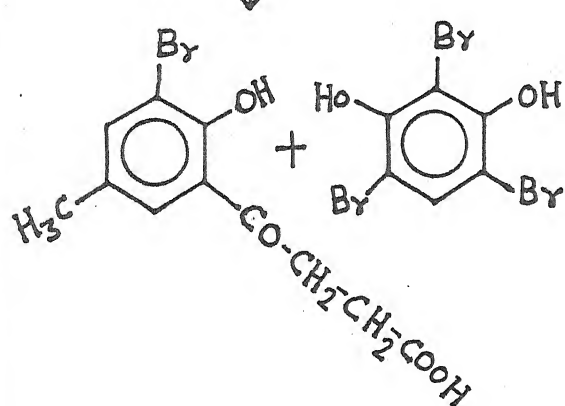
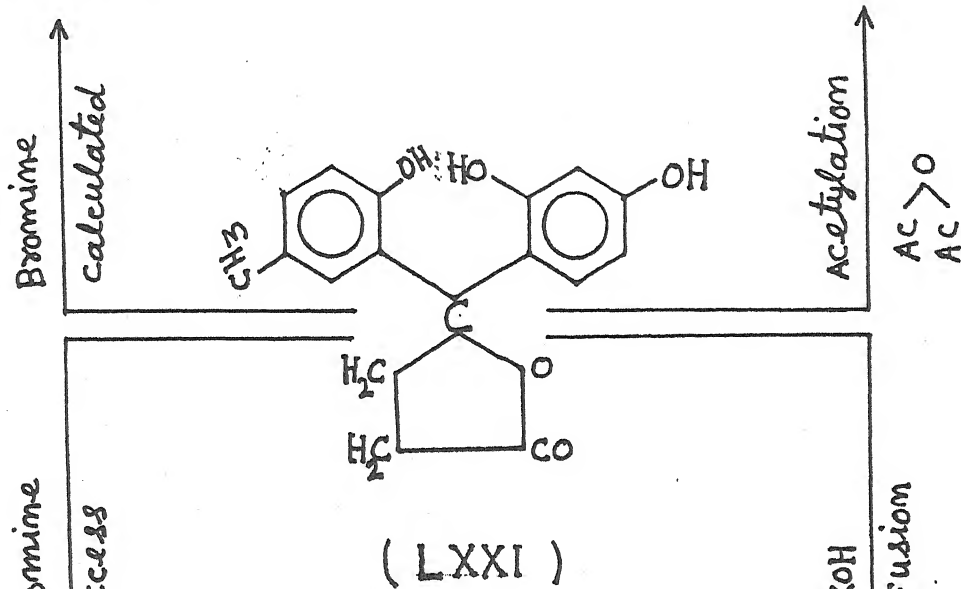
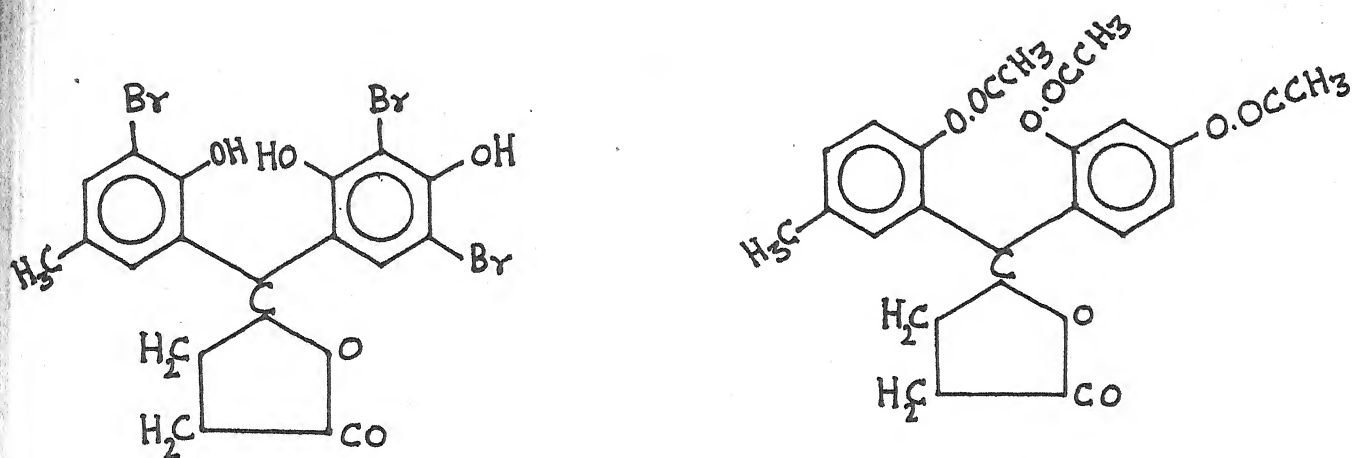


STRUCTURE OF :

5.(B) (2-HYDROXY 5-METHYL PHENYL) RESORCINOL SUCCIN-AS-EIN.

The dye was prepared by condensing β -(2-hydroxy 5-methyl benzoyl) propionic acid with resorcinol in presence of 3-4 drops of conc.sulphuric acid as a condensing agent (page 245). The dye having molecular formula $C_{17}H_{16}O_5$, Mol. wt. 300.0, yielded tri acetyl and tri bromo derivatives on acetylation and bromination (with calculated amount of bromine) respectively. Thus only one resorcinol unit is present in the dye molecule. Caustic potash fusion of the dye gave a molecule of β -(2-hydroxy 5-methyl benzoyl) propionic acid alongwith a molecule of resorcinol. Treatment of the dye with excess of bromine gave mono bromo derivative of the same acid alongwith a molecule of tri bromo resorcinol. On the basis of above chemical evidences the structure (LXXI) has been assigned to the dye molecule.

All the above reactions are shown in the chart F (page 118).

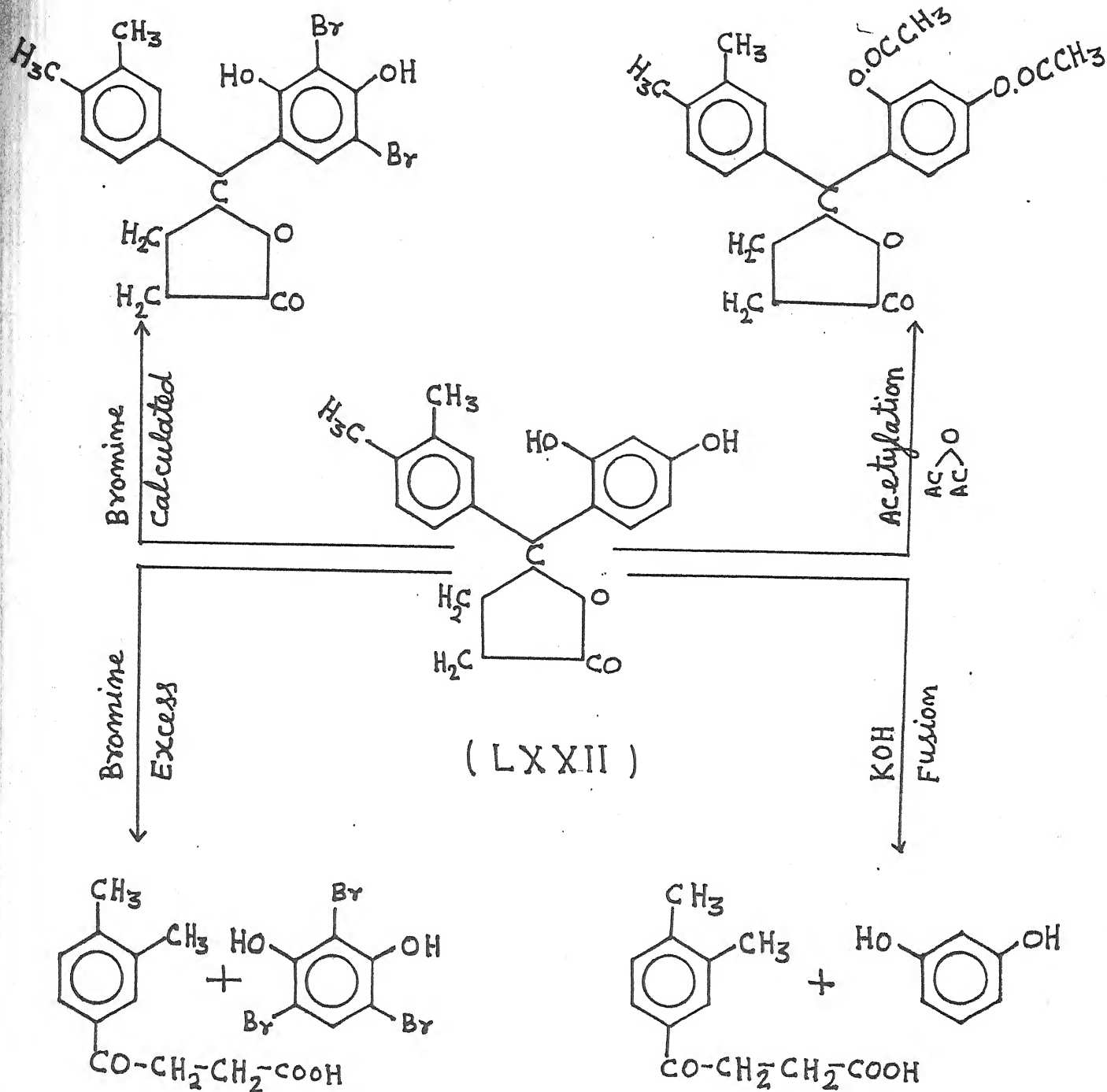


STRUCTURE OF :

5.(C) (3,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN.

The dye (3,4-dimethyl phenyl) resorcinol succin-as-ein having mol.for. $C_{18}H_{18}O_4$, Mol.wt. 298.0 was prepared by condensing β -(3,4-dimethyl benzoyl) propionic acid with resorcinol in presence of few drops of conc.sulphuric acid as the condensing agent (page 255). The dye gave diacetyl and dibromo derivatives on acetylation and bromination (with calculated amount of bromine) respectively. Thus only one molecule of resorcinol is present in the dye molecule. The dye on treatment with excess of bromine yielded the β -(3,4-dimethyl benzoyl) propionic acid and a molecule of tribromo resorcinol. Caustic potash fusion of the dye yielded the same acid alongwith a molecule of resorcinol. On the basis of the above chemical evidences the dye was assigned the structure (LXXII).

All the reactions are shown in the chart G (page 120).



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EXPERIMENTAL

PREPARATION OF DYES FROM ACIDS

The dyes have been prepared by condensing the various γ -keto acids (1 to 14 given on page 63) with different phenols taken in slight excess than molecular proportion in presence of minimum quantity of concentrated sulphuric acid. The resulting dyes when tested to detect the presence of sulphur, gave negative test. This shows that dyes were not sulphonated in presence of minimum quantity of sulphuric acid.

Phenolphthalein and Fluorescein have been prepared by condensing phthalic anhydride with phenol and resorcinol respectively in presence of few drops (3-6) of concentrated sulphuric acid. The above two dyes have been used for making comparison with the dyes derived from different γ -keto acids which were obtained by applying Friedel-Crafts reaction using phthalic anhydride or substituted phthalic anhydride or succinic anhydride and an appropriate aromatic compound.

Similarly phenolphthalein, fluorescein and succinein analogues have been prepared by condensing tetrachloro phthalic anhydride, nitro phthalic anhydride and succinic anhydride respectively with phenol and resorcinol and these have been compared with the dyes derived from acids which were prepared by applying Friedel-Crafts reaction using tetrachloro phthalic anhydride or nitro phthalic anhydride or succinic anhydride and different mono-substituted or disubstituted aromatic compounds i.e.

2-chloro aniline, methyl salicylate, p-cresol and o-xylene.

Chapter III, IV, V and VI includes dyes derived from α -keto acids of series-A (page 63), series-B (page 63), series-C (page 63), and series-D (page 63) respectively.

IR spectra were recorded by using Perkin Elemer infrared (KBr) and NMR was recorded on varian A-60, TMS as internal reference and solvents CDCl_3 , $\text{CD}_3\text{-CO-CD}_3$ and DMSO, were used and the chemical shift have been given in τ (Tou) values.

The purity of a dye was checked by TLC or paper chromatography. In case of TLC, methanol has been used as the solvent and in case of paper chromatography butanol saturated with ammonia has been used as the mobile phase and 1% caustic soda solution as the developing agent.

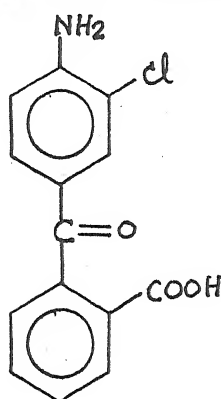
The analytical data are given in percentage.

CHAPTER -III

The chapter III includes the dyes derived from the following acids:-

- (1) O-(4-amino 3-chloro benzoyl) benzoic acid.
- (2) O-(3-carbmethoxy 4-hydroxy benzoyl) benzoic acid.
- (3) O-(2-hydroxy 5-methyl benzoyl) benzoic acid.
- (4) O-(3,4-dimethyl benzoyl) benzoic acid.

DYES DERIVED FROM O-(4-AMINO 3-CHLORO BENZOYL) BENZOIC ACID :



O-(4-Amino 3-chloro benzoyl) benzoic acid.

The acid¹⁻³ was prepared by carrying out Friedel-crafts reaction between 2-chloro aniline (dry A.R. 85ml.) and phthalic anhydride (14.6gm., about 0.1 mole) in presence of anhydrous aluminium chloride (27gm., about 0.2 mole) as catalyst. The yield of the acid was 18.2 gm. excess of 2-chloro aniline was used to serve as the solvent.

The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a reflux condenser connected with a gas absorption trap. The reaction was carried out below 20°C by adding anhydrous aluminium

chloride in portions, when the vigorous reaction subsided, the mixture was heated on boiling water bath until the evolution of hydrogen chloride gas ceased practically.

The heavy dark coloured complex was decomposed by adding 25ml of concentrated hydrochloric acid (in about 200ml ice cold water). The excess of 2-chloro aniline was removed by steam distillation. The residue was extracted 3-4 times with hot boiling 10% solution of sodium carbonate and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from methanol, m.p. $177-179^{\circ}\text{C}$. The white needle shaped crystalline acid is soluble in hot water, methanol ethanol, chloroform and acetone.

Anal.for : $\text{C}_{14}\text{H}_{10}\text{NClO}_3$ (Mol.wt.= 275.5)

Calc. : C, 60.98; H, 3.63; N, 5.08; Cl, 12.89;

Found : C, 60.92; H, 3.61; N, 5.06; Cl, 12.85;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (about 1.0g) and fused sodium acetate (3.6g) were refluxed with 18ml of freshly distilled acetic anhydride at $130-140^{\circ}\text{C}$ for four hours. The hot contents were poured in a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of cream coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot.

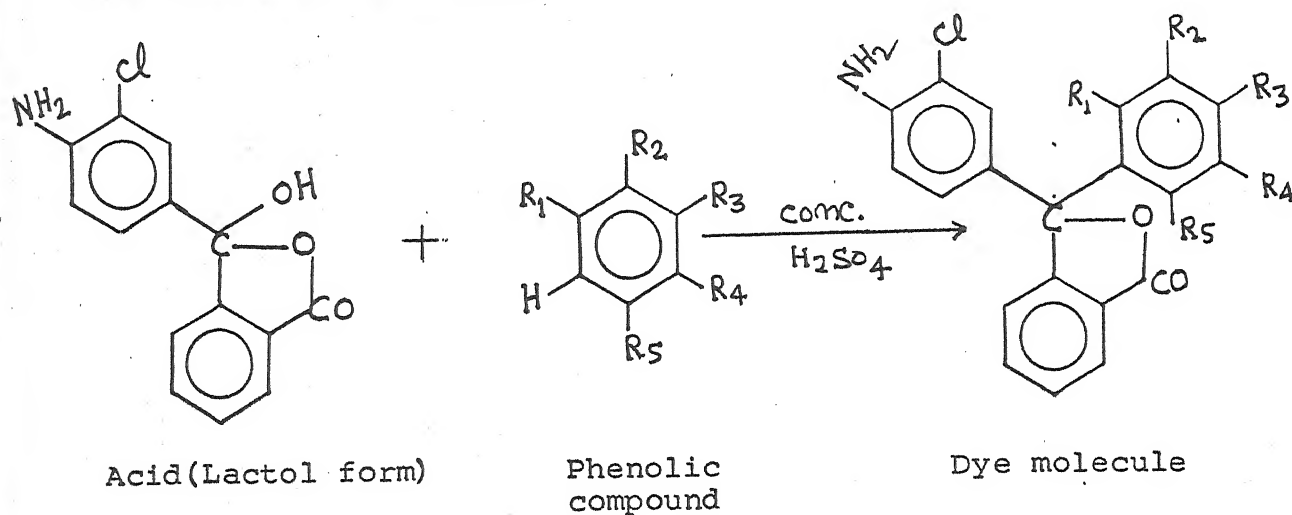
It was finally crystalized from acetone, yield 0.72gm, m.p. 264-265°C. It is soluble in chloroform, acetone and acetic acid.

Anal.for. : $C_{18}H_{14}NClO_5$ or $C_{14}H_8NClO_3(COCH_3)_2$; Mol.wt.= 359.5

Calc. : C, 60.08; H, 3.89; N, 3.89; Cl, 9.87; acetyl, 23.92;

Found : C, 59.98; H, 3.87; N, 3.86; Cl, 9.83; acetyl, 23.81;

The dyes prepared from the acid may be represented by the following structure.



DYES :

(4-amino 3-chloro phenyl) phenol phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

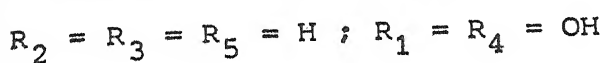
(4-amino 3-chloro phenyl) resorcinol phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

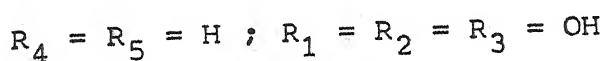
(4-amino 3-chloro phenyl) catechol phthal-as-ein.

$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

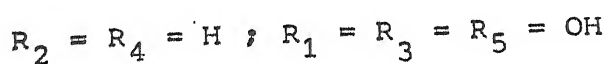
(4-amino 3-chloro phenyl) hydroquinone phthal-as-ein.



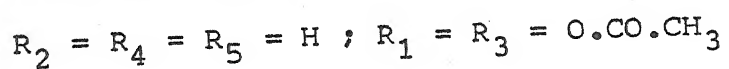
(4-amino 3-chloro phenyl) pyrogallol phthal-as-ein.



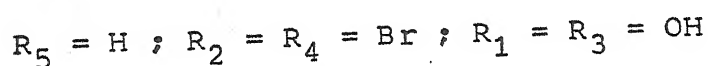
(4-amino 3-chloro phenyl) phloroglucinol phthal-as-ein.



(4-acetyl amino 3-chloro phenyl) diacetyl resorcinol phthal-as-ein.



(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol phthal-as-ein.



(4-AMINO 3-CHLORO PHENYL) PHENOL PHTHAL-AS-EIN :

An intimate mixture of the acid (2.5gm) and phenol (2.0gm), slight excess than the molecular proportion, was taken in the hard boiling tube and heated in an oil bath to make the contents homogeneous. 4-5 drops of concentrated sulphuric acid were then added and heating was continued at 160-170°C for five and half hours till the melten mass of the tube become brittle on cooling. The condensed mass was taken out from the tube and subjected to steam distillation to remove excess of phenol. The buff colour solid mass left in the flask was powdered and extracted with 2% sodium hydroxide solution. It was filtered and the dye was precipitated from the buff coloured filtrate by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallization from

rectified spirit and dried in vacuum desiccator, yield 2.2g, m.p. 140-141°C.

The buff dye is soluble in ethanol and rectified spirit. The ethanolic solution is almost brownish-red in colour and on adding a drop of alkali it becomes pink in colour.

The purity of the dye was tested by paper chromatography adopting technique 1A, 1B.

Paper	Whatman No.1
Mobile phase	Butanol saturated with ammonia.
Developing agent	1% aqueous caustic soda.
Reference dye	Phenolphthalein.

A 25x10 Cm strip was taken and a very dilute solution of the dye was spotted on the paper (on a base line, 4 Cm from one end) with a micro syringe. Similarly a dilute aqueous solution of reference dye was also spotted on the base line at a distance of about 3 Cm from former spot. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed chromatogram, each dye gave only one corresponding pink spot. This confirmed the homogeneity and purity of the dye.

Found : Rf (Phenolphthalein), 0.93;

Rf (4-amino 3-chloro phenyl) phenol phthal-as-ein, 0.94;

Reported : Rf (Phenolphthalein), 0.92;

Anal.for : $C_{20}H_{14}NClO_3$ (Mol.wt.= 351.5)

Calc. : C, 68.28; H, 3.98; N, 3.98; Cl, 10.10;

Found : C, 68.22; H, 3.96; N, 3.95; Cl, 10.04;

(4-AMINO 3-CHLORO PHENYL) RESORCINOL PHTHAL-AS-EIN :

Homogenised mixture of the acid (6.0g) and resorcinol (3.0g), excess than molecular proportion, was heated in an oil bath to 120°C to make it homogeneous and 5-6 drops of concentrated sulphuric acid were added. The contents were heated at 145-160°C for about four hours, till the molten mass become hard and brittle on cooling. The condensed mass was crushed and washed well with water to remove excess of resorcinol. It was extracted with 2% aqueous caustic soda solution and filtered. The dye was precipitated from reddish-brown with green fluorescent filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 100°C and then in a vacuum desiccator, yield 5.4g.

The dye is red, crystalline in nature, m.p. 275-277°C. The ethanolic solution is golden yellow with green fluorescence in colour. On addition of a drop of alkali colour changes from golden yellow to reddish yellow with green fluorescence. In strong basic medium the green fluorescence becomes more intense.

Anal. for.: $C_{20}H_{14}NClO_4$; (Mol. wt. = 367.5)

Calc. : C, 65.31; H, 3.81; N, 3.81; Cl, 9.66;

Found : C, 65.24; H, 3.79; N, 3.78; Cl, 9.62;

(4-AMINO 3-CHLORO PHENYL) CATECHOL PHTHAL-AS-EIN :

A well ground mixture of the acid (2.0g) and catechol (1.5g) was heated in an oil bath at 110°C to make it homogeneous. Few drops (5-6) of conc. sulphuric acid were added and heating was continued at $115-130^{\circ}\text{C}$ for about four hours till the hard brittle mass was obtained on cooling. The isolation and purification were done as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein, yield 1.8g.

The dye is black, crystalline in nature, m.p. $>360^{\circ}\text{C}$. Its ethanolic solution is brown in colour, which changes from black to brownish-black on addition of a drop of alkali. With 2% caustic soda solution gives black colour.

Anal.for. : $\text{C}_{20}\text{H}_{14}\text{NClO}_4$ (Mol.wt.= 367.5)

Calc. : C, 65.31; H, 3.81; N, 3.81; Cl, 9.66;

Found : C, 65.23; H, 3.78; N, 3.77; Cl, 9.61;

(4-AMINO 3-CHLORO PHENYL) HYDROQUINONE PHTHAL-AS-EIN :

A well ground mixture of the acid (2.0g) and hydroquinone (1.5g) was heated to make it homogeneous. A few (5-6) drops of concentrated sulphuric acid were added and the mixture was heated for four hours at $160-175^{\circ}\text{C}$. The isolation and purification of the dye were done as in case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein. The dye is black crystalline in nature decomposes above 300°C . It is soluble in ethanol

methanol, chloroform and acetic acid. The ethanolic solution is golden brown which turns into leaf brown on addition of a drop of alkali.

Anal.for. : $C_{20}H_{14}NClO_4$ (Mol.wt.=367.5)

Calc. : C, 65.31; H, 3.81; N, 3.81; Cl, 9.66;

Found : C, 65.24; H, 3.78; N, 3.79; Cl, 9.62;

(4-AMINO 3-CHLORO PHENYL) PYROGALLOL PHTHAL-AS-EIN :

The acid (2.0g) and pyrogallol (1.5g) were intimately mixed and heated in an oil bath to make it homogeneous. A few drops (4-5) of concentrated sulphuric acid were added as condensing agent and the heating was carried out at 125-145°C for four hours till the brittle mass was obtained on cooling. The isolation and purification of the dye were done as described under (4-amino 3-chloro phenyl) resorcinol phthal-as-ein, yield 1.5g.

The black crystalline dye decomposes above 300°C. Its ethanolic solution is wine red which gives violet colour on addition of a drop of alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal.for. : $C_{20}H_{14}NClO_5$ (Mol.wt.=383.5)

Calc. : C, 62.58; H, 3.65; N, 3.65; Cl, 9.26;

Found : C, 62.50; H, 3.61; N, 3.62; Cl, 9.21;

(4-AMINO 3-CHLORO PHENYL) PHLOROGLUCINOL PHTHAL-AS-EIN :

The acid (2.0g) and phloroglucinol (1.5g) were intimately mixed and heated in an oil bath to make it homogeneous. A few drops (4-5) of concentrated sulphuric acid were added as condensing agent and the heating was carried out at 190-210°C for four hours. The dye was isolated and purified in the same manner as described under (4-amino 3-chloro phenyl) resorcinol phthal-as-ein. The dark orange dye is soluble in acetone, ethanol, and acetic acid, yield 1.8g, m.p. >360°C. It gives golden yellow colour in ethanol which turns into reddish orange on addition of a drop of alkali. Strong basic medium also shows dark orange colour.

Anal.for. : $C_{20}H_{14}NClO_5$ (Mol.wt.= 383.5)

Calc. : C, 62.58; H, 3.65; N, 3.65; Cl, 9.26;

Found : C, 62.48; H, 3.62; N, 3.63; Cl, 9.22;

ACETYLATION OF (4-AMINO 3-CHLORO PHENYL) RESORCINOL PHTHAL-AS-EIN :

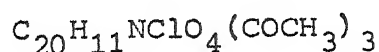
[(4-acetyl amino 3-chloro phenyl) diacetyl resorcinol phthal-as-ein]

The dye (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (1.0g) and fused sodium acetate (3.0g) with 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at 125-135°C for about four hours. The hot contents were then poured slowly into a beaker containing a slush of ice

and water with constant stirring. It was left overnight where upon a light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallised from aqueous ethanol and little acetic acid. It was dried in an oven at 40°C and then over phosphorous pentaoxide under reduced pressure, yield 0.65g.

The acetylated product is pale yellow and has micro crystalline nature, m.p. $175-176^{\circ}\text{C}$. It is soluble in ethanol, acetone, chloroform and acetic acid.

Anal.for. : $\text{C}_{26}\text{H}_{20}\text{NClO}_7$ (Mol.wt.= 493.5) or



Calc. : C, 63.22; H, 4.05; N, 2.84; Cl, 7.19; acetyl, 26.14;

Found : C, 63.16; H, 4.03; N, 2.83; Cl, 7.15; acetyl, 26.08;

BROMINATION OF (4-AMINO 3-CHLORO PHENYL) RESORCINOL
PHthal-AS-EIN :

[(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol
phthal-as-ein]

The resorcinol dye (1.5g) was dissolved in a minimum quantity of glacial acetic acid. 15ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed $120-130^{\circ}\text{C}$ for an hour contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled. It was filtered and washed well with water containing acetic acid and finally with hot water to remove

excess of bromine. It was dissolved in dilute aqueous caustic soda and filtered. The filtrate gave bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallization from aqueous ethanol and dried at 80°C in an oven, and then in vacuum dessiccator, yield 1.2g.

The pale orange coloured dye, soluble in methanol, ethanol acetone and acetic acid has, m.p. $252-253^{\circ}\text{C}$.

Anal.for. : $\text{C}_{20}\text{H}_{11}\text{NClBr}_3\text{O}_4$ (Mol.wt. 604.5)

Calc. : Br, 39.70;

Found : Br, 39.62;

CAUSTIC POTASH TREATMENT OF (4-AMINO 3-CHLORO PHENYL)
RESORCINOL PHTHAL-AS-EIN :

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated on a sand bath with a few drops of water in order to make it paste. The dye (1.0g) was then added to it. The contents were heated for about four hours, till the dark red colour of dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. The dark red residue (I) settled down on just neutralising the excess of alkali. It was filtered and washed well with water. The filtrate when acidified further by adding excess of dilute hydrochloric acid, gave white precipitate (II) which was filtered and washed with water. It was crystallised from

aqueous ethanol and dried in a vacuum dessiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent a brownish red residue (III) was obtained.

Identification of residue (I) :

It was identified as the unreacted residual dye, giving all colour reactions of the dye it self and it was further confirmed by mixed melting point determination with the original dye.

Identification of residue (II) :

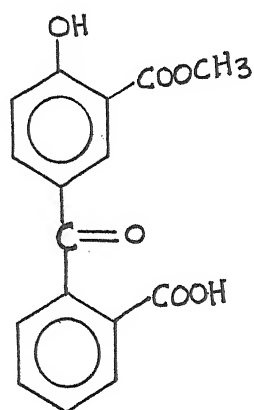
The compound, m.p. $177-179^{\circ}\text{C}$, gave the usual test of carboxylic group alongwith the dye test for amino group and was identified to be O-(4-amino 3-chloro benzoyl) benzoic acid and was confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of residue (III) :

The purified substance, m.p. at $109-111^{\circ}\text{C}$, gave positive test with ferric chloride solution, Tollen's reagent and Fehling solution. It responded to fluorescein test with phthalic anhydride. On the basis of these observations the residue (III) was identified as resorcinol. It was further confirmed by mixed melting point determination with the authentic sample of resorcinol.

Bromination, acetylation and caustic potash fusion of the dye are shown in chart A (page 105).

2. DYES DERIVED FROM O-(3-CARBMETHOXY 4-HYDROXY BENZOYL) BENZOIC ACID:



O-(3-Carbmethoxy 4-hydroxy benzoyl)benzoic acid.

The acid¹⁻³ was prepared by carrying out Friedel crafts reaction between methyl salicylate (dry A.R. 80ml), and phthalic anhydride (14.6g, 0.1 mole) in presence of anhydrous aluminium chloride (27.0g, 0.2 mole) in a similar manner as O-(4-amino 3-chloro benzoyl) benzoic acid. The acid was crystallised from hot water in the form of white crystalline solid, m.p. 170-172°C. The acid is soluble in water, benzene, ether, chloroform and acetone, yield 15.0g.

Anal.for. : $C_{16}H_{12}O_6$ (Mol.wt.=300)

Calc. : C, 64.00; H, 4.00;

Found : C, 63.84; H, 3.96;

PREPRATION OF ACETYL DERIVATIVE OF THE ACID :

The acetyl derivative of the acid was prepared by

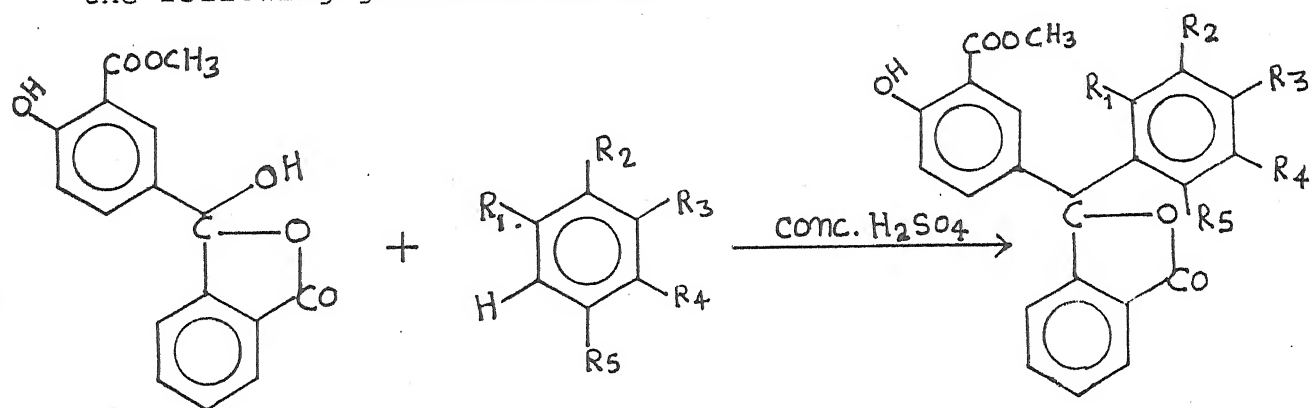
taking (1.3g) acid, (4.0g) of fused sodium acetate and 15ml of acetic anhydride in a similar manner as in the preparation of acetyl derivative of ortho (4-amino 3-chloro benzoyl) benzoic acid (page 128). The coloured acetyl derivated was treated with animal charcoal till decolourised and finally recrystallised from acetone. The yield 1.1g, m.p.112°C(Decomposed). It is soluble in acetone, chloroform and acetic acid.

Anal.for. : $C_{20}H_{16}O_8$ or $C_{16}H_{10}O_6(COCH_3)_2$ (Mol.wt.=384)

Calc. : C,62.50; H,4.17; acetyl,22.40;

Found : C,62.39; H,4.14; acetyl,22.34;

The dyes prepared from the acid may be represented by the following general formula:-



Acid(Lactol form)

Phenolic compound

Dye molecule

DYES:

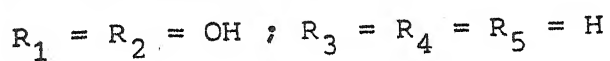
(3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

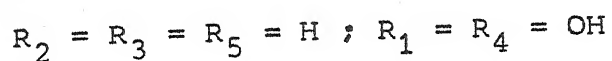
(3-carbmethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

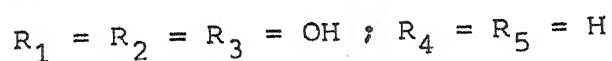
(3-carbmethoxy 4-hydroxy phenyl) catechol phthal-as-ein.



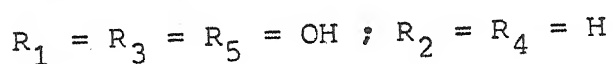
(3-carbmethoxy 4-hydroxy phenyl) hydroquinone phthal-as-ein.



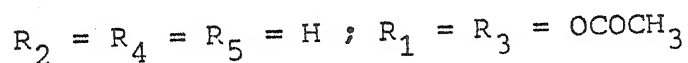
(3-carbmethoxy 4-hydroxy phenyl) pyrogallol phthal-as-ein.



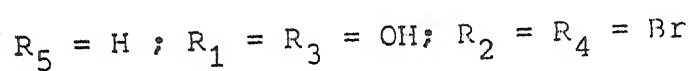
(3-carbmethoxy 4-hydroxy phenyl) phloroglucinol phthal-as-ein.



(4-acetoxy 3-carbmethoxy phenyl) diacetyl resorcinol phthal-as-ein



(3-bromo 5-carbmethoxy 4-hydroxy phenyl) dibromo resorcinol phthal-as-ein.



(3-CARBMETHOXY 4-HYDROXY PHENYL) PHENOL PHTHAL-AS-EIN :

The dye was prepared by condensing the acid (1.5g) and phenol (1.2g) in presence of few (4-5) drops of concentrated sulphuric acid. The heating was carried out for four hours at 175-180°C, till brittle mass was obtained on cooling. Excess of phenol was removed by steam distillation. The mass left in the flask was powdered and extracted with 2% sodium hydroxide solution. It was filtered and the dye was precipitated from coloured filtrate by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum desiccator, yield 1.3g.

The orange coloured dye has m.p. 126-127°C. Its ethanolic solution is brownish-red in colour, which turns into pink on adding a drop of alkali.

Anal.for. : $C_{22}H_{16}O_6$ (Mol.wt.= 376)

Calc. : C, 70.21; H, 4.26;

Found : C, 70.18; H, 4.23;

(3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL PHTHAL-AS-EIN :

The dye was prepared by condensing the acid (5.2g) and resorcinol (2.5g) in presence of 6-7 drops of concentrated sulphuric acid. Heating was continued for four and half hours at 125-135°C, till brittle mass was obtained on cooling. The isolation and purification were done as in the case of (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein, ^(page 141) yield 4.6g.

The red microcrystalline dye having m.p. 182-184°C is soluble in benzene chloroform ethanol and methanol. Its ethanolic solution is golden yellow with green fluorescence and turns into reddish yellow with green fluorescence on adding a drop of alkali. In strong basic medium it gives reddish brown colour with green fluorescence.

Anal.for. : $C_{22}H_{16}O_7$ (Mol.wt.= 392)

Calc. : C, 67.35; H, 4.08;

Found : C, 67.26; H, 4.06;

(3-CARBMETHOXY 4-HYDROXY PHENYL) CATECHOL PHTHAL-AS-EIN :

The dye was prepared by condensing the acid (1.5g) and catechol (1.1g) in presence of conc. sulphuric acid (3-4 drops) at the temp. $120-130^{\circ}\text{C}$ for four hours, till the molten mass of the tube become hard brittle on cooling. The isolation and purification were done as in the case of (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein, (page 141), yield 1.2g.

The dye is black in colour, m.p. above 360°C . Its ethanolic solution is brown in colour which turns into brownish black on adding a drop of alkali.

Anal. for. : $\text{C}_{22}\text{H}_{16}\text{O}_7$ (Mol. wt. = 392)

Calc. : C, 67.35; H, 4.08;

Found : C, 67.38; H, 4.05;

(3-CARBMETHOXY 4-HYDROXY PHENYL) HYDROQUINONE PHTHAL-AS-EIN :

The dye was prepared by heating the homogeneous mixture of the acid (1.5g) and hydroquinone (1.0g) in an oil bath at the temp. $160-180^{\circ}\text{C}$ for about four hours in presence of 3-4 drops of concentrated sulphuric acid. The isolation and purification were done similarly as in the case of (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein (page 141), yield 1.4g.

The black coloured dye decomposes above 300°C . Its ethanolic solution is crimson (light brown) in colour. It gives brown colour on addition of alkali. It is soluble in ethanol,

methanol and acetic acid.

Anal.for. : $C_{22}H_{16}O_7$ (Mol.wt.= 392)

Calc. : C, 67.35; H, 4.08;

Found : C, 67.27; H, 4.06;

(3-CARBMETHOXY 4-HYDROXY PHENYL) PYROGALLOL PHTHAL-AS-EIN :

It was prepared by carrying out the condensation of homogeneous mixture of the acid (1.5g) and pyrogallol (1.0g) in an oil bath in presence of 3-4 drops of conc. sulphuric acid at the temperature $130-145^{\circ}C$ for about four hours. The isolation and purification were done as described in the case of (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein, (page 141), yield 1.2g.

The black shining crystalline dye, decomposes above $320^{\circ}C$. It is soluble in ethanol, methanol and acetic acid. Its ethanolic solution is wine red in colour, which turns into blue violet on adding a drop of alkali.

Anal.for. : $C_{22}H_{16}O_8$ (Mol.wt.= 408)

Calc. : C, 64.71; H, 3.92;

Found : C, 64.63; H, 3.89;

(3-CARBMETHOXY 4-HYDROXY PHENYL) PHLOROGLUCINOL PHTHAL-AS-EIN:

An intimate mixture of the acid (1.5g) and phloroglucinol (1.2g) was heated in an oil bath to make it homogeneous

and then 3-4 drops of conc. sulphuric acid were added and heating was continued for about four hours at 190-210°C. The isolation and purification of the dye were done in a similar manner as described in the case of (3-carbmethoxy 4-hydroxy phenyl) phenol phthal-as-ein (page 141), yield 1.3g.

The dark orange coloured dye having m.p. above 360°C. Its ethanolic solution is golden yellow in colour, which turns into reddish orange on addition of a drop of alkali. It is soluble in ethanol, methanol, acetone and acetic acid.

Anal.for. : $C_{22}H_{16}O_8$ (Mol.wt.= 408)

Calc. : C, 64.71; H, 3.92;

Found : C, 64.64; H, 3.90;

ACETYLATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL)
RESORCINOL PHTHAL-AS-EIN :

[(4-acetoxy 3-carbmethoxy phenyl)diacetyl resorcinol phthal-as-ein]

The dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein (1.0g) and fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml), were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed in an oil bath at 120-130°C for four hours. The isolation purification and crystallisation were done in a similar manner as described in the acetylation of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 135). The acetylated compound was dried in an oven at 80°C and then over phosphorous penta-oxide under reduced pressure, yield 0.75g.

The acetylated product is light yellow in colour, m.p. 200-202°C, soluble in ether, methanol, chloroform and acetic acid.

Anal.for. : $C_{28}H_{22}O_{10}$ or $C_{22}H_{13}O_7(OC.CH_3)_3$ (Mol.wt.= 518)

Calc. : C, 64.86; H, 4.25; acetyl, 24.90

Found : C, 64.75; H, 4.22; acetyl, 24.85

BROMINATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL PHTHAL-AS-EIN :

[(3-bromo 5-carbmethoxy 4-hydroxy phenyl) dibromo resorcinol phthal-as-ein]

The dye (3-carbmethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein (1.0g) was brominated, isolated and purified in a similar manner as in the bromination of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 136), yield 0.82g.

The pale-orange coloured dye has m.p. 256-257°C. Its ethanolic solution is light orange in colour. In moderate and strong basic mediums it gives deep orange colour with green fluorescence.

Anal.for. : $C_{22}H_{13}Br_3O_7$ (Mol.wt.=629)

Calc. : Br, 38.16; Found : Br, 38.08;

CAUSTIC POTASH TREATMENT OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL PHTHAL-AS-EIN :

Caustic potash treatment of the resorcinol dye (1.0g) was carried out in an identical manner as in the case of

(4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 137).
As a result of fusion three residues were obtained.

Identification of Residue - I :

It was identified and confirmed as the unreacted residual dye from its colour reactions and mixed melting point determination with the authentic sample of the dye.

Identification of Residue - II :

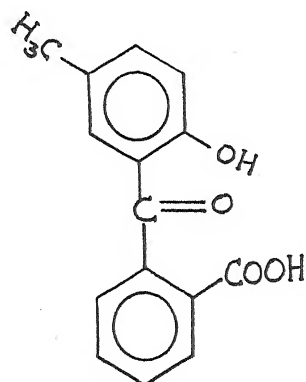
It was recrystallised from acetone, m.p. $170-172^{\circ}\text{C}$.
It was acidic in nature and gave positive tests for carboxyl and phenolic groups. It was identified to be O-(3-carbomethoxy 4-hydroxy benzoyl) benzoic acid and confirmed by mixed melting point determination and superimposition of the IR spectra with the authentic sample.

Identification of Residue - III :

The purified sample melted at $109-110^{\circ}\text{C}$. It gave positive test with Fehling's solution, ferric chloride, amonical silver nitrate. It gave fluorescein test with phthalic anhydride on the basis of these observations it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are shown in chart-B (page 108).

3. DYES DERIVED FROM O-(2-HYDROXY 5-METHYL BENZOYL) BENZOIC ACID:



[O-(2-Hydroxy 5-methyl benzoyl) benzoic acid]

The acid¹⁻³ was prepared by carrying out Friedel-Crafts reaction between p-cresol (dry AR 85ml) and phthalic anhydride (15.5g about 0.1 mole) and anhydrous aluminium chloride (27.0g, 0.2 mole) used as a catalyst in a similar manner as O-(4-amino 3-chloro benzoyl) benzoic acid (page 127). The acid was crystallised from acetone m.p. 182-183°C. It is soluble in hot water, acetone and methanol, yield 16.0g.

Anal.for. : $C_{15}H_{12}O_4$ (Mol.wt. = 256)

Calc. : C, 70.31; H, 4.69;

Found : C, 70.22; H, 4.67;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (1.2g) and sodium acetate, fused (3.5g) were refluxed with 15ml of freshly distilled acetic anhydride at 120-130°C for four hours. The hot contents were poured in a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of brown coloured

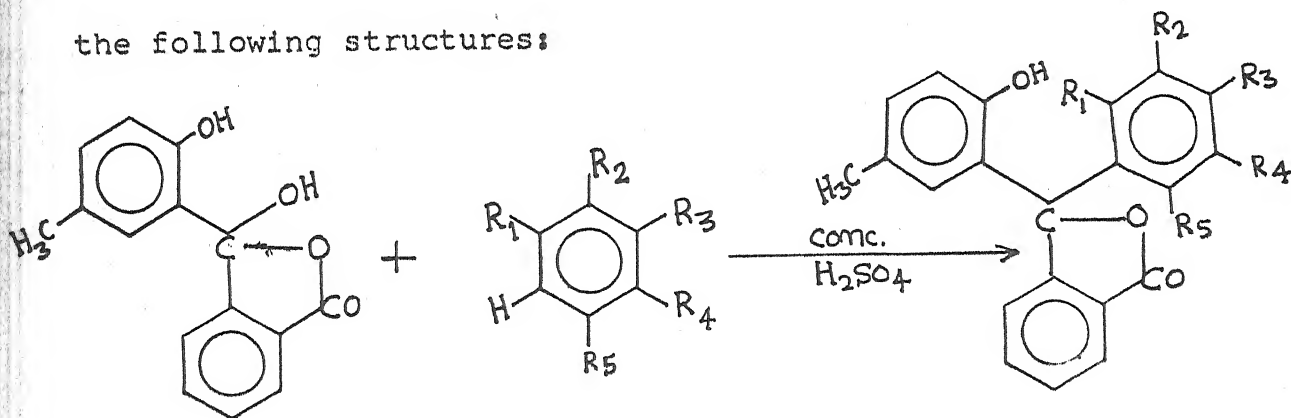
solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of light brown solid, m.p. 190°C . It is soluble in acetone, chloroform and acetic acid, yield 0.98g.

Anal.for. : $\text{C}_{19}\text{H}_{16}\text{O}_6$ or $\text{C}_{15}\text{H}_{10}\text{O}_4(\text{OC}\cdot\text{CH}_3)_2$ (Mol.wt.=340)

Calc. : C, 67.06; H, 4.71; acetyl, 25.29;

Found : C, 66.97; H, 4.69; acetyl, 25.21;

The dyes prepared from the acid may be represented by the following structures:



Acid (Lactol form)

Phenolic compound.

Dye molecule.

DYES:

(2-hydroxy 5-methyl phenyl) phenol phthal-as-ein.

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$; $\text{R}_3 = \text{OH}$

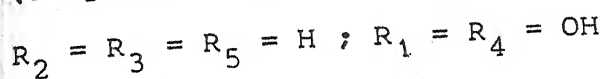
(2-hydroxy 5-methyl phenyl) resorcinol phthal-as-ein.

$\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$; $\text{R}_1 = \text{R}_3 = \text{OH}$

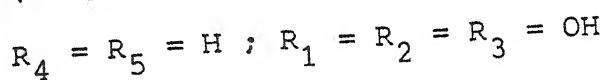
(2-hydroxy 5-methyl phenyl) catechol phthal-as-ein.

$\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{H}$; $\text{R}_1 = \text{R}_2 = \text{OH}$

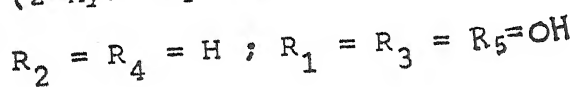
(2-hydroxy 5-methyl phenyl) hydroquinone phthal-as-ein.



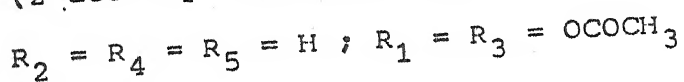
(2-hydroxy 5-methyl phenyl) pyrogallol phthal-as-ein.



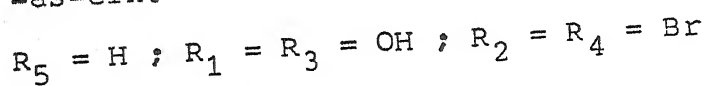
(2-hydroxy 5-methyl phenyl) phloroglucinol phthal-as-ein.



(2-acetoxy 5-methyl phenyl) diacetyl resorcinol phthal-as-ein.



(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol phthal-as-ein.



(2-HYDROXY 5-METHYL PHENYL) PHENOL PHTHAL-AS-EIN:

An intimate mixture of the acid (1.5g) and phenol (1.2g) was condensed in an oil bath in presence of concentrated sulphuric acid (3-4 drops) at 160-170°C for about four and half hours till a brittle mass was obtained on cooling. Excess of phenol was removed by steam distillation. The reddish pink solid mass left in the flask was extracted with 2% sodium hydroxide solution. It was filtered and dye was precipitated from the coloured filtrate by gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in a vacuum desiccator, yield 1.3g.

The pinkish red coloured micro crystalline dye has,

m.p. 182-184°C. The ethanolic solution of the dye is light yellow in colour which turns into pink on adding a drop of alkali. In strong basic medium it gives intense pink colour.

Anal.for. : $C_{21}H_{16}O_4$ (Mol.wt.=332)

Calc. : C, 75.90; H, 4.82;

Found : C, 75.79; H, 4.78;

(2-HYDROXY 5-METHYL PHENYL) RESORCINOL PHTHAL-AS-EIN :

It was prepared by condensing acid (5.0g) and resorcinol (2.6g) on the oil bath in presence of concentrated sulphuric acid (5-6 drops) at 140-160°C for about four and half hours. The isolation and purification were carried out in a same manner as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 132), yield 4.52g.

The dark orange dye having m.p. 290-292°C, is soluble in benzene, ethanol and methanol. It dissolves in ethanol giving golden yellow colour with green fluorescence, which turns into reddish yellow colour with green fluorescence on adding a drop of alkali.

Anal.for. : $C_{21}H_{16}O_5$ (Mol.wt.=348)

Calc. : C, 72.41; H, 4.60;

Found : C, 72.33; H, 4.58;

(2-HYDROXY 5-METHYL PHENYL) CATECHOL PHTHAL-AS-EIN :

It was prepared by heating the mixture of the acid

(1.65g) and catechol (1.3g) in an oil bath at 120-130°C for four and half hours in presence of 3-4 drops of concentrated sulphuric acid. The isolation and purification of the dye were done in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 132), yield 1.3g.

The black dye having, m.p. >360°C, is soluble in benzene, ethanol, methanol and acetic acid. It gives brown colour in ethanol which turns into brownish black on adding a drop of alkali.

Anal.for. : $C_{21}H_{16}O_5$ (Mol.wt.348)

Calc. : C, 72.41; H, 4.60;

Found : C, 72.31; H, 4.57;

(2-HYDROXY 5-METHYL PHENYL) HYDROQUINONE PHTHAL-AS-EIN :

Acid (2.0g) and hydroquinone (1.5g) were heated in an oil bath at 160-180°C for four hours in presence of few drops of concentrated sulphuric acid. The isolation and purification were carried out in a same manner as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 132), yield 1.8g.

The black coloured dye, decomposed at 320°C, is soluble in ethanol, methanol, chloroform and acetic acid. Its ethanolic solution is crimson in colour which turns into dark brown on adding a drop of alkali.

Anal.for. : $C_{21}H_{16}O_5$ (Mol.wt.=348)

Calc. : C, 72.41; H, 4.60;

Found : C, 72.34; H, 4.56;

(2-HYDROXY 5-METHYL PHENYL) PYROGALLOL PHTHAL-AS-EIN :

The mixture of acid (2.0g) pyrogallol (1.6g) and 4-5 drops of concentrated sulphuric acid, was heated in an oil bath at 130-140°C, for about four hours. The isolation and purification were carried out in a similar manner as in case of (4-amino 3-chloro phenyl) resorcinol, ^{Phthal-as-ein,} (page 132), yield 2.6g.

The black coloured dye having m.p. above 360°C gives wine red colour in ethanol which turns into blue violet on adding a drop of alkali.

Anal.for. : $C_{21}H_{16}O_6$ (Mol.wt.=364)

Calc. : C, 69.23; H, 4.40;

Found : C, 69.17; H, 4.38;

(2-HYDROXY 5-METHYL PHENYL) PHLOROGLUCINOL PHTHAL-AS-EIN :

The mixture of acid (2.0g), phloroglucinol (1.5g) and few drops (2-3) of concentrated sulphuric acid was heated in an oil bath at 190-200°C for about four hours. The isolation and purification were carried out in a similar manner as in case of (4-amino 3-chloro phenyl) ^{resorcinol} phthal-as-ein, yield 2.2g.

The orange coloured dye m.p. 320-322°C gives yellow colour in ethanol which turns into dark red on adding a drop of alkali.

Anal.for. : $C_{21}H_{16}O_6$ (Mol.wt.=364)

Calc. : C, 69.23; H, 4.40;

Found : C, 69.18; H, 4.37;

ACETYLATION OF (2-HYDROXY 5-METHYL PHENYL)
RESORCINOL PHTHAL-AS-EIN :

[(2-acetoxy 5-methyl phenyl) diacetyl resorcinol phthal-as-ein]

Starting with (1.0g) of the dye (3.0g) of the fused sodium acetate and 15ml of freshly distilled acetic anhydride, the acetyl derivative was prepared exactly in a similar manner as in the acetylation of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 135). The yellow acetyl derivative was treated with animal charcoal and finally crystallised from aq. ethanol in presence of a drop of acetic acid, yield 0.8g.

The yellow coloured triacetyl derivative having m.p. 188-189°C, is soluble in benzene, ethanol, methanol, chloroform and acetic acid.

Anal.for. : $C_{27}H_{22}O_8$ or $C_{21}H_{13}O_5(OC.CH_3)_3$ (Mol.wt.=474)

Calc. : C, 68.35; H, 4.64; acetyl, 27.22;

Found : C, 68.28; H, 4.61; acetyl, 27.15;

BROMINATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL
PHTHAL-AS-EIN :

[(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol phthal-as-ein]

The dye, (2-hydroxy 5-methyl phenyl) resorcinol phthal-as-ein (1.0g) was dissolved in a minimum quantity of glacial acetic acid, 10ml of 10% solution of bromin in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at

120-130°C for an hour. The isolation and purification were carried out in a similar manner as in the case of bromination of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein, (page 136), yield 0.82g.

The orange crystalline dye having m.p. 250-251°C, is soluble in benzene, ether, chloroform and acetone. Its ethanolic solution is red in colour which turns into reddish pink with green fluorescence on addition of alkali.

Anal.for. : $C_{21}H_{13}Br_3O_5$ (Mol.wt.= 585)

Calc. : Br, 41.03; Found : Br, 40.95;

CAUSTIC POTASH TREATMENT OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL PHTHAL-AS-EIN :

Caustic potash treatment of the resorcinol dye (1.0g) was carried out in an identical manner as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 137). As a result of fusion three residues were obtained.

Identification of Residue - I :

It was identified and confirmed as the unreacted residual dye from its colour reactions and mixed melting point determination with the authentic sample of dye.

Identification of Residue - II :

It was recrystallised from acetone, m.p. 182-184°C. It gave positive tests for carboxyl and phenolic groups and was

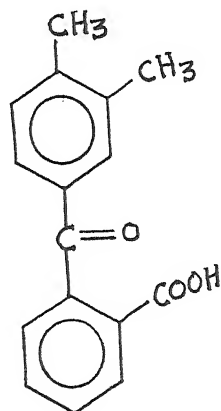
identified and confirmed as O-(2-hydroxy 5-methyl benzoyl) benzoic acid by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue - III :

The purified sample melted at 108-109°C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammonical silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are shown in chart C (page 111).

4. DYES DERIVED FROM O-(3,4-DIMETHYL BENZOYL) BENZOIC ACID :



[O-(3,4-dimethyl benzoyl) benzoic acid.]

The acid¹⁻³ was prepared by carrying out Friedel-Crafts reaction between orthoxylene (dry AR 100ml) and phthalic anhydride (19.5g, 0.1 mole) and anhydrous aluminium chloride (27g, 0.2 mole) used as a catalyst, in a similar manner as in O-(4-amino 3-chloro benzoyl) benzoic acid (page 127). The white crystalline acid was crystallised from acetone, m.p. 153-154°C, yield 15g. It is soluble in ether, acetone and methanol.

Anal.for. : $C_{16}H_{14}O_3$ (Mol.wt.=254)

Calc. : C, 75.59; H, 5.51;

Found : C, 75.51; H, 5.48;

PREPARATION OF ACETYL DERIVATIVE OF ACID :

The acid (1.2g) and fused sodium acetate (3.5g) were refluxed with 20ml of freshly distilled acetic anhydride in an identical manner as in the acetylation of O-(4-amino 3-chloro benzoyl) benzoic acid (page 128). The coloured acetyl derivative

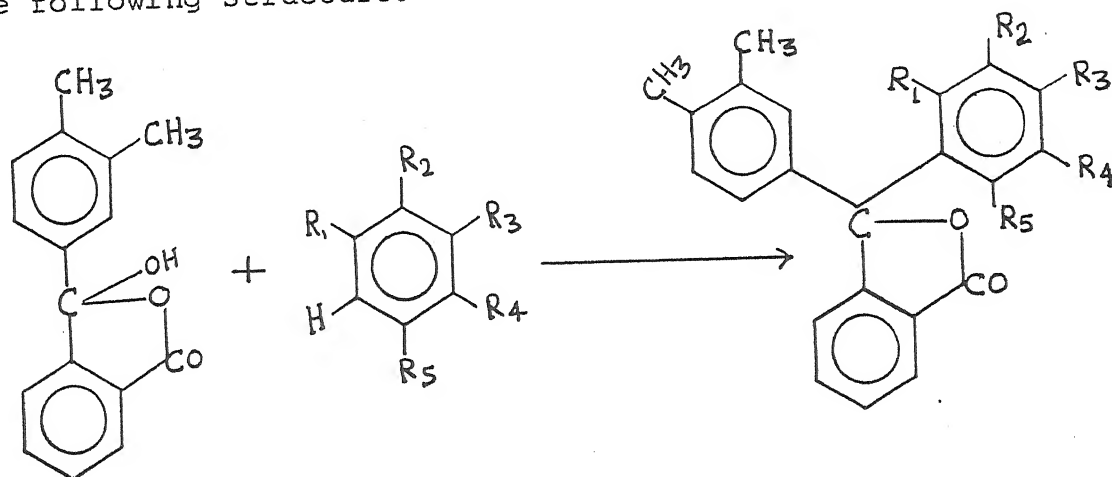
was decolourised by treating with animal charcoal. It was crystallised from acetone in the form of amorphous solid, m.p. 85-87°C. It is soluble in acetone, chloroform and acetic acid, yield 0.75g.

Anal.for. : $C_{18}H_{16}O_4$ or $C_{16}H_{13}O_3(OC.CH_3)$ (Mol.wt.=296)

Calc. : C, 72.97; H, 5.41; acetyl, 14.53;

Found : C, 72.90; H, 5.38; acetyl, 14.49;

The dyes prepared from the acid may be represented by the following structure:



Acid(Lactol form)

Phenolic compound.

Dye molecule.

DYES:

(3,4-dimethyl phenyl) phenol phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

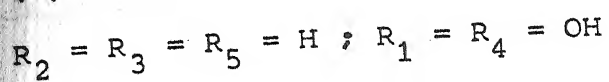
(3,4-dimethyl phenyl) resorcinol phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

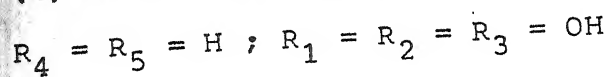
(3,4-dimethyl phenyl) catechol phthal-as-ein.

$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

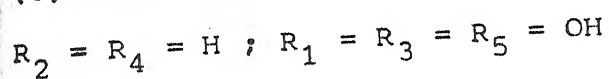
(3,4-dimethyl phenyl) hydroquinone phthal-as-ein.



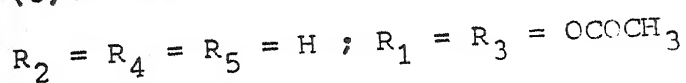
(3,4-dimethyl phenyl) pyrogallol phthal-as-ein.



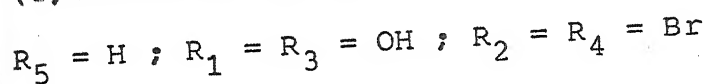
(3,4-dimethyl phenyl) phloroglucinol phthal-as-ein.



(3,4-dimethyl phenyl) diacetyl resorcinol phthal-as-ein.



(3,4-dimethyl phenyl) dibromo resorcinol phthal-as-ein.



(3,4-DIMETHYL PHENYL) PHENOL PHTHAL-AS-EIN :

The acid (1.5g) and phenol (1.0g) was condensed in an oil bath in presence of concentrated sulphuric acid (4-5 drops) at $160-170^{\circ}C$ for about four and half hours in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 132), yield 1.3g.

The brown coloured dye is micro crystalline in nature, m.p. $178-180^{\circ}C$. Its ethanolic solution is light yellow in colour, which turns into pink on adding a drop of alkali. It is soluble in benzene, acetone and ethanol.

Anal.for. : $C_{22}H_{18}O_3$ (Mol.wt.=330)

Calc. : C, 80.00; H, 5.45;

Found : C, 79.92; H, 5.42;

3,4-DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN :

It was prepared by condensing the intimate mixture of acid (5.0g) and resorcinol (3.0g) on the oil bath in presence of few drops of concentrated sulphuric acid at 140-150°C for about four and half hours. The extraction and purification was carried out in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein, yield 5.6g.

The orange yellow micro crystalline dye having m.p. 155-157°C, is soluble in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is yellow with green fluorescence in colour which turns into brownish yellow with green fluorescence on adding a drop of alkali. In strong basic medium the reddish-brown colour is obtained.

Anal.for. : $C_{22}H_{18}O_4$ (Mol.wt.=346)

Calc. : C, 76.30; H, 5.20;

Found : C, 76.19; H, 5.18;

(3,4-DIMETHYL PHENYL) CATECHOL PHTHAL-AS-EIN :

The dye was prepared by heating the homogeneous mixture of the acid (2.0g) and catechol (1.5g) in an oil bath at 120-130°C for about four hours in the presence of few drops of concentrated sulphuric acid. The isolation and purification of the dye were done as in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 132), yield 1.8g.

The dye is black in colour, m.p. above 360°C . Its ethanolic solution is light brown in colour. It gives deep black colour on addition of alkali. It is soluble in acetone, ethanol and acetic acid.

Anal.for. : $\text{C}_{22}\text{H}_{18}\text{O}_4$ (Mol.wt.=346)

Calc. : C, 76.30; H, 5.20;

Found : C, 76.22; H, 5.17;

(3,4-DIMETHYL PHENYL) HYDROQUINONE PHTHAL-AS-EIN :

It was prepared by condensing the homogeneous mixture of the acid (2.5g) and hydroquinone (1.5g). The intimate mixture was heated in an oil bath in presence of 3-5 drops of conc. sulphuric acid for about four hours at $120-130^{\circ}\text{C}$, till the molten mass become hard and brittle on cooling. The isolation and purification were carried out in a similar manner as in case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 132) yield 2.1g.

The black coloured dye having m.p. above 360°C , is soluble in chloroform ethanol and methanol. Its ethanolic solution gives golden yellow colour which turns into dark brown on addition of alkali.

Anal.for. : $\text{C}_{22}\text{H}_{18}\text{O}_4$ (Mol.wt.346)

Calc. : C, 76.30; H, 5.20;

Found : C, 76.21; H, 5.15;

(3,4-DIMETHYL PHENYL) PYROGALLOL PHTHAL-AS-EIN :

The mixture of acid (2.0g), pyrogallol (1.2g) and 3-5 drops of concentrated sulphuric acid, was heated in an oil bath at 130-150°C for about four hours. The dye was isolated and purified exactly in a similar manner as the other dyes, yield 2.3g.

The black shining crystalline dye having m.p. above 360°C, is soluble in ethanol, methanol and acetic acid. It dissolves in ethanol giving wine red colour which turns into violet on adding a drop of alkali.

Anal.for. : $C_{22}H_{18}O_5$ (Mol.wt.=362)

Calc. : C, 72.93; H, 4.97;

Found : C, 72.84; H, 4.93;

(3,4-DIMETHYL PHENYL) PHLOROGLUCINOL PHTHAL-AS-EIN :

It was prepared by the condensing the intimate mixture of acid (2.5g) and phloroglucinol (1.5g) on an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 190-210°C for about four hours. Isolation and purification of the dye were done as in the case of other dyes, yield 2.8g.

The dark brown dye m.p. >360°C, gives lemon yellow colour with ethanol, which turns into orange on adding a drop of alkali. It is soluble in acetone ethanol, methanol and acetic acid.

Anal.for. : $C_{22}H_{18}O_5$ (Mol.wt.=362)

Calc. : C, 72.93; H, 4.97;

Found : C, 72.81; H, 4.92;

ACETYLATION OF (3,4-DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN:

[(3,4-dimethyl phenyl) diacetyl resorcinol phthal-as-ein]

The dye (3,4-dimethyl phenyl) resorcinol phthal-as-ein (1.0g) was acetylated, ^{and the product was} isolated and purified exactly in a similar manner as described in the acetylation of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 135), yield 0.72g.

The crystalline acetyl derivative is light yellow coloured and has, m.p. 110-112°C. It is soluble in benzene, ether, chloroform and acetic acid.

Anal.for. : $C_{26}H_{22}O_6$ or $C_{22}H_{16}O_4(OC.CH_3)_2$ (Mol.wt.=430)

Calc. : C, 72.56; H, 5.12; acetyl, 20.00;

Found : C, 72.47; H, 5.08; acetyl, 19.94;

BROMINATION OF (3,4-DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN:

[(3,4-dimethyl phenyl) dibromo resorcinol phthal-as-ein]

The dye (3,4-dimethyl phenyl) resorcinol phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic acid and 15ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130°C

for an hour. The isolation and purification of the compound were carried out in a similar manner as in the case of bromination of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 134), yield 0.80g.

The dirty orange crystalline compound having m.p. 88-89°C, is soluble in benzene, ether, chloroform, acetone and acetic acid.

Anal.for. : $C_{22}H_{16}Br_2O_4$ (Mol.wt.=504)

Calc. : Br, 31.75; Found : Br, 31.68;

CAUSTIC POTASH TREATMENT OF (3,4-DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN :

For caustic potash treatment of (3,4-dimethyl phenyl) resorcinol phthal-as-ein identical procedure was followed as described in the case of (4-amino 3-chloro phenyl) resorcinol phthal-as-ein (page 137). It gave following three residues:

Identification of Residue - I :

It was identified and confirmed to be unreacted dye from its colour reactions and determination of the mixed melting point with authentic sample.

Identification of Residue - II :

It was acidic in nature and gave positive tests for carboxylic group. It was identified to be O-(3,4-dimethyl benzoyl)

benzoic acid and confirmed by mixed melting point determination (m.p. 153-154°C) and by superimposition of the IR spectra with the authentic sample.

Identification of Residue - III :

The purified sample melted at 109-110°C. It gave positive tests with ferric chloride, Fehling's solution and ammonical silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations it was confirmed to be resorcinol.

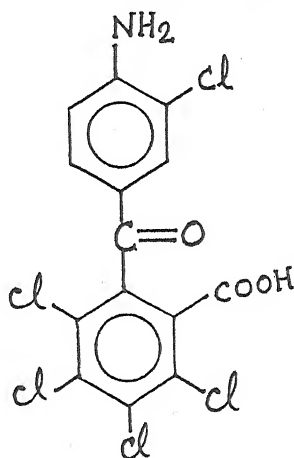
Acetylation, bromination and caustic potash treatment of the dye are shown in chart D (page 114).

CHAPTER - IV

Chapter IV includes the dyes derived from the following acids:-

- (1) O-(4-amino 3-chloro benzoyl) tetra chloro benzoic acid.
- (2) O-(3-carbomethoxy 4-hydroxy benzoyl) tetra chloro benzoic acid.
- (3) O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid.
- (4) O-(3,4-dimethyl benzoyl) tetra chloro benzoic acid.

1. DYES DERIVED FROM O-(4-AMINO 3-CHLORO BENZOYL) TETRA CHLORO BENZOIC ACID :



O-(4-amino 3-chloro benzoyl)tetra chloro benzoic acid.

The acid⁴⁻⁸ was prepared by carrying out Friedel-Crafts reaction between 2-chloro aniline (dry AR 85ml) and tetra chloro phthalic anhydride (28g. about 0.1 mole) in presence of anhydrous aluminium chloride (27.0g, 0.2 mole) as catalyst.

The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trape. The reaction was carried out below 40°C by adding anhydrous aluminium chloride in portions. When the vigorous reaction subsided, the mixture was heated on boiling water bath until the evolution of hydrogen chloride ceased.

The heavy, dark brown coloured complex was decomposed by adding 30ml of concentrated hydrochloric acid (in 250ml ice cold water). The excess of 2 chloro aniline was removed by steam distillation. The residue was extracted 3-4 times with hot boiling 10% solution of sodium carbonate and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallised from acetone, m.p. 180°C (decomposed), yield 24.2g. The grey crystalline acid is soluble in acetone and methanol.

Anal.for. : $\text{C}_{14}\text{H}_6\text{NCl}_5\text{O}_3$ (Mol.wt.=413.5)

Calc. : C,40.63, H,1.45; N,3.39; Cl,42.93;

Found : C,40.54; H,1.43; N,3.36; Cl,42.87;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (1.0g) and fused sodium acetate (3.0g) were refluxed with 15ml of freshly distilled acetic anhydride at $120-130^{\circ}\text{C}$ for four hours. The hot contents were poured in a beaker containing ice cold water with constant stirring. The

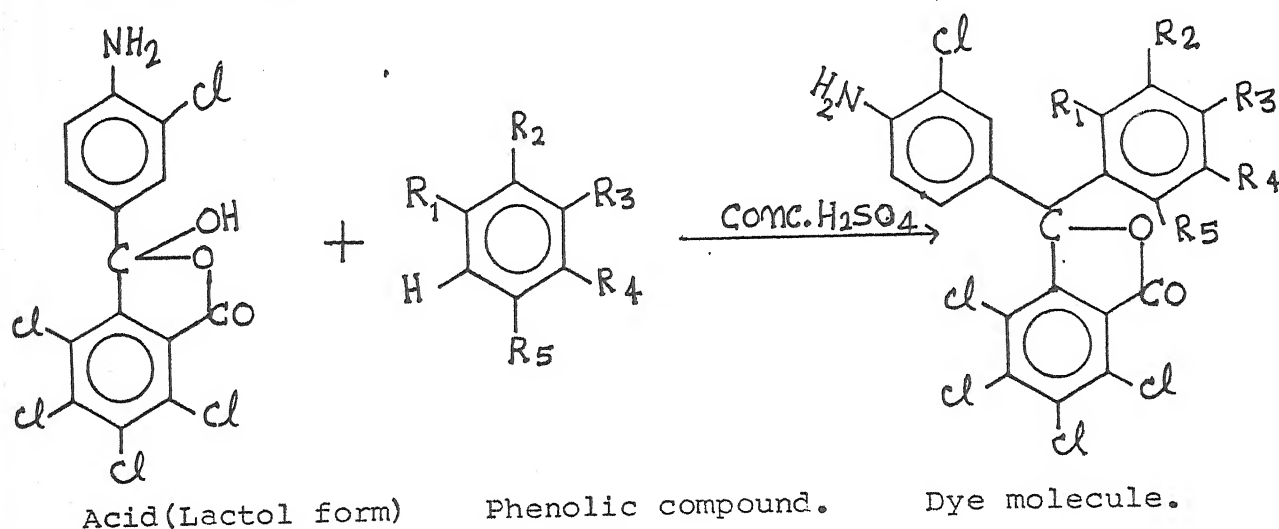
acetyl derivative settled down in the form of brown coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of brown solid, decomposed at 110°C . It is soluble in acetone, methanol chloroform and acetic acid, yield 0.62g.

Anal.for. : $\text{C}_{18}\text{H}_{10}\text{NCl}_5\text{O}_5$ or $\text{C}_{14}\text{H}_4\text{NCl}_5\text{O}_3(\text{OCCH}_3)_2$ (Mol.wt.497.5)

Calc. : C, 43.42; H, 2.01; N, 2.81; Cl, 35.68; acetyl, 17.29;

Found : C, 43.34; H, 1.98; N, 2.78; Cl, 35.61; acetyl, 17.23;

The dyes prepared from the acid may be represented by the following structure:



DYES:

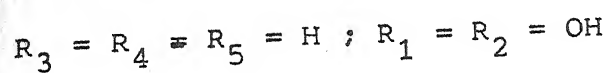
(4-amino 3-chloro phenyl) phenol tetra chloro phthal-as-ein.

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$; $\text{R}_3 = \text{OH}$

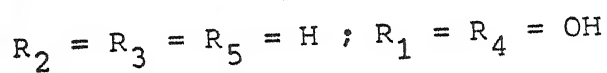
(4-amino 3-chloro phenyl) resorcinol tetra chloro phthal-as-ein.

$\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$; $\text{R}_1 = \text{R}_3 = \text{OH}$

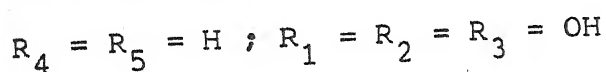
(4-amino 3-chloro phenyl) catechol tetra chloro phthal-as-ein.



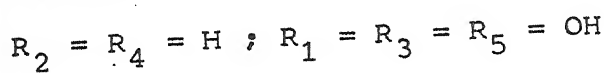
(4-amino 3-chloro phenyl) hydroquinone tetra chloro phthal-as-ein.



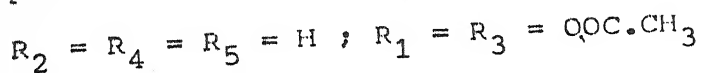
(4-amino 3-chloro phenyl) pyrogallol tetra chloro phthal-as-ein.



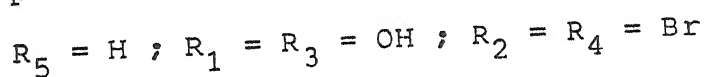
(4-amino 3-chloro phenyl) phloroglucinol tetra chloro phthal-as-ein.



(4-acetylamino 3-chloro phenyl) diacetyl resorcinol tetra chloro phthal-as-ein.



(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol tetra chloro phthal-as-ein.



(4-AMINO 3-CHLORO PHENYL) PHENOL TETRA CHLORO PHTHAL-AS-EIN:

An intimate mixture of the acid (2.6g) and phenol (2.0g) (slight excess than the molecular proportion) was taken in a hard boiling tube and heated in an oil bath to make it homogeneous. A few drops (3-4) of concentrated sulphuric acid were added and heating was continued at 160-175°C for about four and half hours. Isolation and purification were carried out in a similar way in the case of (4-amino 3-chloro phenyl) phenol phthal-as-ein (page 131), yield 2.4g.

The orange brown coloured dye, having m.p. 258-260°C is soluble in alcohol and acetic acid. Its ethanolic solution is light yellow in colour which turns into violet on adding a drop of alkali.

The purity of the dye was tested by paper chromatography adopting technique^{1A,1B}.

Paper	Whatman No.1
Mobile phase	Butanol saturated with ammonia.
Developing agent	1% aqueous caustic soda.
Reference dye	Phenolphthalein.

A 25x10 Cm strip was taken and a very dilute ethanolic solution of the dye was spotted on the paper (on a base line, 4 Cm from one end) with a micro syringe. Similarly a dilute aqueous solution of reference dye was also spotted on the base line at a distance of about 3 Cm from the former spot. The mobile phase was allowed to run for thirteen hours. The paper then taken out, dried and sprayed with 1% aqueous alkaline solution. After drying the sprayed chromatogram, each dye gave only one corresponding pink spot. This confirmed the homogeneity and purity of (4-amino 3-chloro phenyl) phenol tetrachloro phthal-as-ein.

Found : Rf (Phenolphthalein), 0.92

Rf [(4-amino 3-chloro phenyl) phenol tetrachloro
phthal-as-ein], 0.94

Reported: Rf (Phenolphthalein), 0.91

Anal.for. : $C_{20}H_{10}NCl_5O_3$ (Mol.wt.489.5)

Calc. : C,49.03; H,2.04; N,2.86; Cl,36.26;

Found : C,48.97; H,2.01; N,2.83; Cl,36.21;

(4-AMINO 3-CHLORO PHENYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN:

A well ground acid (5.5g) and resorcinol (2.5g) was heated in an oil bath to $115^{\circ}C$ to make it homogeneous. A few drops (4-5) of concentrated sulphuric acid were added and the contents were stirred well. The heating was continued at $140-160^{\circ}C$ for about four and half hours, till the molten mass become hard and brittle on cooling. The condensed mass was crushed and washed well with water to remove the excess of resorcinol. It was extracted with 2% aqueous caustic soda solution and filtered. The dye was precipitated as a golden brown dye with green fluorescence by adding slowly of dilute hydrochloric acid with constant stirring. The dye was purified by crystallisation from rectified spirit, dried in an oven at $80^{\circ}C$ and then in a vacuum desiccator, yield 5.1g.

The lemon yellow crystalline dye has m.p. $290-292^{\circ}C$. Its ethanolic solution is pale cream which turns into light orange with green fluorescence. The green fluorescence becomes more intense on addition of 2% caustic soda solution. It is soluble in chloroform, ethanol, methanol and acetic acid.

Anal.for. : $C_{20}H_{10}NCl_5O_4$ (Mol.wt.= 505.5)

Calc. : C,47.48; H,1.98; N,2.77; Cl,35.11;

Found : C,47.42; H,1.95; N,2.74; Cl,35.05;

(4-AMINO 3-CHLORO PHENYL) CATECHOL TETRACHLORO PHTHAL-AS-EIN :

An intimate mixture of the acid (2.0g) and catechol (1.2g) was heated in an oil bath at 100°C to make it homogeneous, few drops (3-4) of concentrated sulphuric acid were then added and heating was continued at 120-130°C for about four hours. The isolation and purification of the dye were done in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol tetra chloro phthal-as-ein (page 171), yield 2.1g.

The black crystalline dye decomposed at 250°C, is soluble in acetone, ethanol, methanol and acetic acid. Its ethanolic solution is light brown which turns into golden brown on adding a drop of alkali.

Anal.for. : $C_{20}H_{10}NCl_5O_4$ (Mol.wt.505.5)

Calc. : C, 47.48; H, 1.98; N, 2.77; Cl, 35.11;

Found : C, 47.41; H, 1.94; N, 2.72; Cl, 35.03;

(4-AMINO 3-CHLORO PHENYL) HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

It was prepared by heating the homogeneous mixture of the acid (2.5g) and hydroquinone (1.5g) in an oil bath at 160-180°C for about four hours in presence of concentrated sulphuric acid. The isolation and purification were carried out in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol tetra chloro phthal-as-ein, yield 1.8g.

The black coloured dye (decomposed above 300°C) gives

golden brown colour in ethanol which turns into yellowish-brown on adding a drop of alkali.

Anal.for. : $C_{20}H_{10}NCl_5O_4$ (Mol.wt. 505.5)

Calc. : C, 47.48; H, 1.98; N, 2.77; Cl, 35.11;

Found : C, 47.40; H, 1.93; N, 2.73; Cl, 35.04;

(4-AMINO 3-CHLORO PHENYL) PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by heating the homogeneous mixture of the acid (3.1g) and pyrogallol (2.0g) in an oil bath at 130-140°C. The conc. sulphuric acid 3-4 drops were added and heated for about four hours. The dye was isolated and purified exactly in a similar manner as in the cases of other dyes, yield 3.60g. The black coloured dye (decomposed above 180°C), gives brown colour with ethanol and gives blackish brown and violet colour in moderate and strong basic mediums respectively.

Anal.for. : $C_{20}H_{10}NCl_5O_5$ (Mol.wt. 521.5)

Calc. : C, 46.02; H, 1.92; N, 2.68; Cl, 34.04;

Found : C, 45.94; H, 1.89; N, 2.64; Cl, 33.97;

(4-AMINO 3-CHLORO PHENYL) PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The condensation of the intimate mixture of acid (2.5g) phloroglucinol (2.0g) was carried out in presence of 4-6 drops of conc. sulphuric acid at 190-200°C for about four hours. Isolation and purification of the dye were done as in the cases of other dyes, yield 2.8g.

The grey coloured dye (decomposed above 300°C) gives grey colour with ethanol, which turns into pale cream on adding a drop of alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal.for. : $\text{C}_{20}\text{H}_{10}\text{NCl}_5\text{O}_5$ (Mol.wt. 521.5)

Calc. : C, 46.02; H, 1.92; N, 2.68; Cl, 34.04;

Found : C, 45.93; H, 1.90; N, 2.65; Cl, 33.98;

ACETYLATION OF (4-AMINO 3-CHLORO PHENYL) RESORCINOL
TETRACHLORO PHTHAL-AS-EIN :

[(4-acetyl amino 3-chloro phenyl) diacetyl resorcinol ^{tetrachloro} phthal-
-as-ein]

The dye, (4-amino 3-chloro phenyl) resorcinol tetra-chloro phthal-as-ein (1.0g) and fused sodium acetate (3.0g) and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at $120-130^{\circ}\text{C}$ for about four hours. The hot contents were then poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight where upon a buff coloured solid settled ^{down}. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallised from aqueous ethanol and little acetic acid. It was dried in an oven at 60°C and then over phosphorous pentaoxide under reduced pressure, yield 0.72g.

The acetylated product is buff coloured and has microcrystalline nature, m.p. $180-182^{\circ}\text{C}$. It is soluble in benzene, ether, chloroform and acetic acid.

Anal.for. : $C_{26}H_{16}NCl_5O_7$ or $C_{20}H_7NCl_5O_4(OC.CH_3)_3$ (Mol.wt.631.5)

Calc. : C,49.41; H,2.53; N,2.22; Cl,28.11; acetyl,20.43;

Found : C,49.33; H,2.51; N,2.19; Cl,28.06; acetyl,20.36;

BROMINATION OF (4-AMINO 3-CHLORO PHENYL) RESORCINOL
TETRACHLORO PHTHAL-AS-EIN :

[(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol
tetrachloro phthal-as-ein]

The dye, (4-amino 3-chloro phenyl) resorcinol tetra chloro phthal-as-ein (1.0g) was dissolved in a minimum quantity of glacial acetic acid, 10ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at $120-125^{\circ}C$ for an hour. Contents were cooled and diluted with minimum quantity of distilled water. A grey coloured powder settled. It was filtered washed well with water containing acetic acid and finally with hot water to remove excess of bromine. It was dissolved in dilute aqueous caustic soda solution and filtered. The filtrate gave bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallisation from aqueous ethanol, and dried at $80^{\circ}C$ in an oven and then in vacuum desiccator, yield 0.86g.

The grey coloured powdered dye having m.p. $155-157^{\circ}C$ is soluble in benzene methanol, acetone, chloroform and acetic acid.

Anal.for. : $C_{20}H_7NCl_5Br_3O_4$ (Mol.wt. 742.5)

Calc. : Br,32.32;

Found : Br,32.25;

CAUSTIC POTASH TREATMENT OF (4-AMINO 3-CHLORO PHENYL)
RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated on a sand bath with a few drops of water in order to make it paste. The dye (1.0g) was then added to it. The contents were heated for about four and half hours, till the dark red colour of the dye faded completely. After cooling the contents were diluted with 50ml of water. The dark red residue (I) settled down on just neutralising the excess of alkali. It was filtered and washed well with water. The filtrate when acidified further by adding excess of dilute hydrochloric acid, gave white precipitate (II). Which was filtered and washed well with water. It was crystallised from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of solvent a brownish red residue (III) was obtained.

Identification of Residue (I) :

The residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue (II) :

The compound, m.p. 180°C (decompose) gave the usual tests of carboxylic group alongwith the dye test for amino and was identified to be O-(4-amino 3-chloro benzoyl) tetra chloro benzoic acid and was confirmed by mixed melting point

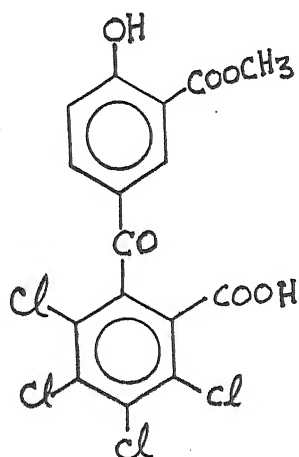
determination and superimposition of IR spectra with the authentic sample.

Identification of Residue (III) :

It was identified as resorcinol having m.p. 109-110°C. It responded to ferric chloride, Fehling's solution test and ammonical silver nitrate, and gave fluorescein test with phthalic anhydride. It was further confirmed by mixed m.p. determination with the authentic sample.

Bromination, acetylation and caustic potash treatment of the dye are shown in chart A (page 105).

2. DYES DERIVED FROM O-(3-CARBMETHOXY 4-HYDROXY BENZOYL)
TETRACHLORO BENZOIC ACID :



O-(3-carbmethoxy 4-hydroxy benzoyl)
tetrachloro benzoic acid.

The acid⁴⁻⁸ was prepared by carrying out Friedel-Crafts reaction between methyl salicylate (dry AR 80ml) and tetrachloro phthalic anhydride (28.5g about 0.1 mole) in presence of anhydrous aluminium chloride (27g about 0.2 mole) as catalyst. The reaction was carried out in a similar manner as in the case of O-(4-amino 3-chloro benzoyl) tetrachloro benzoic acid,^(page 166) yield 20g. The crude acid was crystallized from methanol in the form of cream coloured crystales, m.p. 220°C (decomposed). It is soluble in hot water, ether and methanol.

Anal.for. : $C_{16}H_8Cl_4O_6$ (Mol.wt. 438)

Calc. : C, 43.84; H, 1.83; Cl, 32.42;

Found : C, 43.75; H, 1.81; Cl, 32.37;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

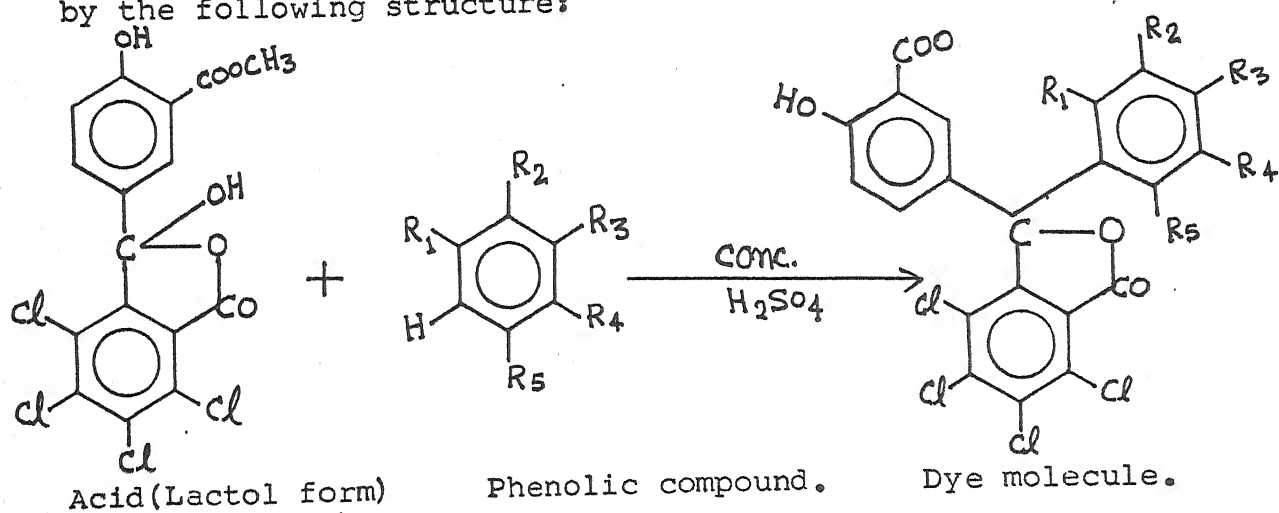
The acid (1.0g) and fused sodium acetate (3.0g) were refluxed with 15ml of freshly distilled acetic anhydride exactly in a similar manner as in the case of acetylation of O-(4-amino 3-chloro benzoyl) tetrachloro benzoic acid (page 167). The brown coloured acetyl derivative having m.p. 207-209°C is soluble in chloroform, acetone and acetic acid.

Anal. for. : $C_{20}H_{12}Cl_4O_8$ or $C_{16}H_6Cl_4O_6(COCH_3)_2$ (Mol. wt. 522)

Calc. : C, 45.98; H, 2.30; Cl, 27.20; acetyl, 16.48;

Found : C, 45.91; H, 2.27; Cl, 27.15; acetyl, 16.42;

The dyes prepared from the acid may be represented by the following structure:



DYES:

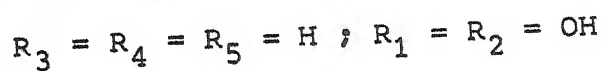
(3-carbomethoxy 4-hydroxy phenyl) phenol tetrachloro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

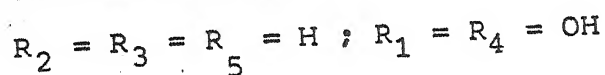
(3-carbomethoxy 4-hydroxy phenyl) resorcinol tetrachloro phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

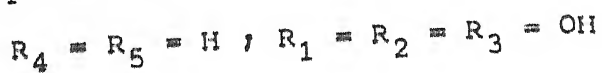
(3-carbomethoxy 4-hydroxy phenyl) catechol tetrachloro phthal-as-ein.



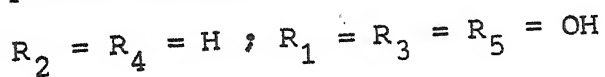
(3-carbomethoxy 4-hydroxy phenyl) hydroquinone tetrachloro phthal-as-ein.



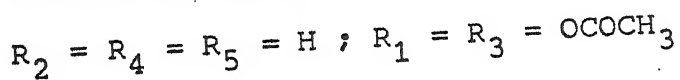
(3-carbomethoxy 4-hydroxy phenyl) pyrogallol tetrachloro phthal-as-ein.



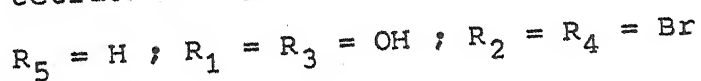
(3-carbomethoxy 4-hydroxy phenyl) phloroglucinol tetrachloro phthal-as-ein.



(4-acetoxy 3-carbomethoxy phenyl) diacetyl resorcinol tetrachloro phthal-as-ein.



(3-bromo 5-carbomethoxy 4-hydroxy phenyl) dibromo resorcinol tetrachloro phthal-as-ein.



(3-CARBOMETHOXY 4-HYDROXY PHENYL) PHENOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (2.0g) and phenol (1.0g) in presence of 3-4 drops of conc. sulphuric acid. The heating, isolation and purification were carried out exactly in a similar manner as in case of (3-carbomethoxy 4-hydroxy phenyl) phenol phthal-as-ein (page 141), yield 1.6g. The orange dye having m.p. 240-242°C gives golden yellow colour

with ethanol, which turns into violet on adding a drop of alkali.

Anal.for. : $C_{22}H_{12}Cl_4O_6$ (Mol.wt. 514)

Calc. : C, 51.36; H, 2.33; Cl, 27.63;

Found : C, 51.29; H, 2.31; Cl, 27.57;

(3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL TETRACHLORO
PHTHAL-AS-EIN :

It was prepared by heating the homogeneous mixture of the acid (5.0g) and resorcinol (3.0g) in an oil bath at $140-160^{\circ}C$. The concentrated sulphuric acid (4-6 drops) was used as a condensing agent. The heating was continued for about four hours. Isolation and purification of the dye were carried out in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol tetrachloro phthal-as-ein (page 169), yield 4.2g.

The light brown shining dye having m.p. $280-282^{\circ}C$, gives pale yellow colour with ethanol, which turns into reddish orange with green fluorescence on adding a drop of alkali. It is soluble in benzene, alcohol and acetic acid.

Anal.for. : $C_{22}H_{12}Cl_4O_7$ (Mol.wt. 530)

Calc. : C, 49.81; H, 2.26; Cl, 26.79;

Found : C, 49.75; H, 2.23; Cl, 26.74;

(3-CARBMETHOXY 4-HYDROXY PHENYL) CATECHOL TETRACHLORO
PHTHAL-AS-EIN :

The condensation of the intimate mixture of acid (3.0g) and catechol (2.0g) was carried out in presence of 4-6 drops of conc. sulphuric acid at 120-130°C for about four hours. Isolation and purification were carried out in a same manner as in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 171), yield 3.6g. The light black coloured dye having m.p. 240-241°C, gives brown colour with ethanol, which turns into blackish-brown on adding a drop of alkali.

Anal. for. : $C_{22}H_{12}Cl_4O_7$ (Mol. wt. 530)

Calc. : C, 49.81, H, 2.26; Cl, 26.79;

Found : C, 49.74; H, 2.24; Cl, 26.75;

(3-CARBMETHOXY 4-HYDROXY PHENYL) HYDROQUINONE TETRACHLORO
PHTHAL-AS-EIN :

The mixture of acid (2.0g) hydroquinone (1.5g) and 3-4 drops of concentrated sulphuric acid, was heated in an oil bath at 160-180°C, for about four hours. The isolation and purification of the dye were done in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, (page 171), yield 1.62g. The black dye having m.p. 300°C (decomposed), gives light brown colour with ethanol, which turns into dark brown on adding a drop of alkali.

Anal. for. : $C_{22}H_{12}Cl_4O_7$ (Mol. wt. 530)

Calc. : C, 49.81; H, 2.26; Cl, 26.79;

Found : C, 49.72; H, 2.23; Cl, 26.74;

(3-CARBMETHOXY 4-HYDROXY PHENYL) PYROGALLOL TETRACHLORO
PHTHAL-AS-EIN :

The mixture of acid (3.0g) pyrogallol (2.0g) and concentrated sulphuric acid (3-5 drops) was heated in an oil bath at 130-140°C for about three and half hours. The isolation and purification were carried out in a same manner as (4-amino 3-chloro phenyl) resorcinol tetra chloro phthal-as-ein, yield 2.5g.

The dye is brown in colour, m.p. above 360°C. It shows wine red colour in ethanol which turns into blue colour on adding a drop of alkali.

Anal.for. : $C_{22}H_{12}Cl_4O_8$ (Mol.wt. 546)

Calc. : C, 48.35; H, 2.20; Cl, 26.00;

Found : C, 48.26; H, 2.18; Cl, 25.95;

(3-CARBMETHOXY 4-HYDROXY PHENYL) PHLOROGLUCINOL TETRACHLORO
PHTHAL-AS-EIN :

The condensation of the intimate mixture of acid (2.0g) phloroglucinol (1.5g) was carried out in presence of 3-4 drops of conc.sulphuric acid at 190-200°C for four hours. Isolation and purification of the dye were done as in the case of other dyes, yield 1.7g.

The dark orange dye decomposed above 300°C. It gives wine red colour with ethanol, which turns into red with green fluorescence on adding a drop of alkali.

Anal.for. : $C_{22}H_{12}Cl_4O_8$ (Mol.wt. 546)

Calc. : C, 48.35; H, 2.20; Cl, 26.00;

Found : C, 48.27; H, 2.17; Cl, 25.92;

ACETYLATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL)
RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

[(4-acetoxy 3-carbmethoxy phenyl) diacetyl resorcinol
tetrachloro phthal-as-ein]

The dye, (3-carbmethoxy 4-hydroxy phenyl) resorcinol tetrachloro phthal-as-ein (1.0g), fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml), were taken in a 50ml round bottom flask fitted with an air condenser. The reaction, isolation and purification were carried out in a similar manner as in the case of acetylation of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 174), yield 0.75g.

The golden brown coloured triacetyl derivative having m.p. 166-168°C, is soluble in benzene, solv. ether, chloroform and acetic acid.

Anal.for. : $C_{28}H_{18}Cl_4O_{10}$ or $C_{22}H_9Cl_4O_7(CO.CH_3)_3$ (Mol.wt. 656)

Calc. : C, 51.22; H, 2.74; Cl, 21.65; acetyl, 19.66;

Found : C, 51.13; H, 2.71; Cl, 21.59; acetyl, 19.60;

BROMINATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL)
RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

[(3-bromo 5-carbmethoxy 4-hydroxy phenyl) dibromo
resorcinol tetrachloro phthal-as-ein]

The dye (1.0g) was dissolved in a minimum quantity of glacial acetic acid, 10ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of dye. The reaction, isolation and purification were carried out in a similar manner as in case of bromination of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, ^(page 175) yield 0.82g.

The pale yellow micro crystalline dye having m.p. 308-309°C, is soluble in solvent ether, alcohol, chloroform and acetic acid.

Anal.for. : $C_{22}H_9Cl_4Br_3O_7$ (Mol.wt. 767)

Calc. : Br, 31.29; Found : Br, 31.23;

CAUSTIC POTASH TREATMENT OF (3-CARBMETHOXY 4-HYDROXY PHENYL)
RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

Caustic potash treatment of the dye (1.0g) was carried out exactly in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, (page 176). As a result following three residues were obtained.

Identification of Residue (I) :

It was identified as unreacted residual dye on the basis of its colour reactions and confirmed by mixed melting

point determination with authentic sample.

Identification of Residue (II) :

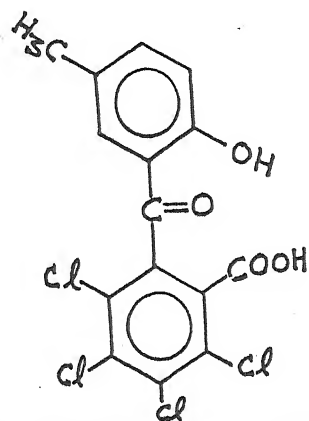
It gives positive test for carboxyl and phenolic groups and was identified and confirmed as O-(3-carbomethoxy 4-hydroxy benzoyl) tetrachloro benzoic acid by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue (III) :

It was identified and confirmed as resorcinol because it gave violet colour with ferric chloride solution, reduced Tollen's reagent and Fehling's solution. It shows no depression in m.p. $108-109^{\circ}\text{C}$ when mixed with the authentic resorcinol sample.

The acetylation bromination and caustic potash fusion of the dye are given in chart B (page 108).

3. DYES DERIVED FROM O-(2-HYDROXY 5-METHYL BENZOYL)
TETRACHLORO BENZOIC ACID :



O-(2-hydroxy 5-methyl benzoyl)
tetrachloro benzoic acid.

The acid⁴⁻⁸ was prepared by carrying out Friedel-Crafts reaction between p-cresol (dry AR 85ml) and tetrachloro phthalic anhydride (28.5g, 0.1 mole) in presence of anhydrous aluminium chloride (27g about 0.2 mole). The yield of the acid was 20.0g. The acid was purified by acetone. The acid having m.p. 230-231°C is soluble in water, acetone and methanol.

Anal.for. : $C_{15}H_8Cl_4O_4$ (Mol.wt. 394)

Calc. : C, 45.69; H, 2.03; Cl, 36.04;

Found : C, 45.61; H, 2.01; Cl, 35.98;

PREPRATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (1.0g) was acetylated exactly in the same way as described in the case of acetylation of O-(4-amino 3-chloro benzoyl) tetrachloro benzoic acid (page 167), yield 0.78g.

The brown coloured diacetyl derivative having m.p.

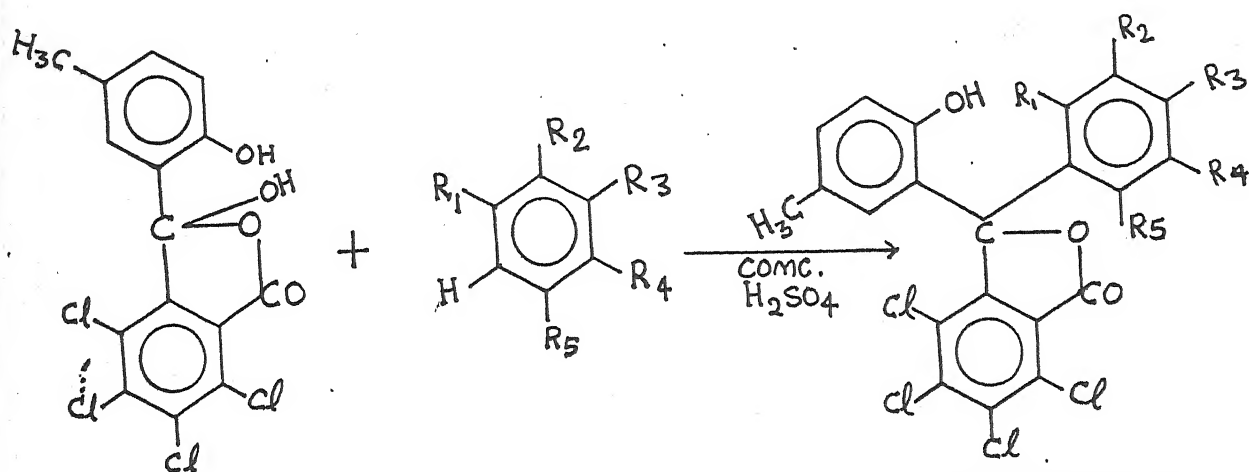
202-203°C is soluble in benzene, acetone, chloroform and acetic acid.

Anal.for. : $C_{19}H_{12}O_6Cl_4$ or $C_{15}H_6Cl_4O_4(COCH_3)_2$ (Mol.wt.478)

Calc. : C, 47.70; H, 2.51; Cl, 29.71; acetyl, 17.99;

Found : C, 47.62; H, 2.48; Cl, 29.66; acetyl, 17.92;

The dyes prepared from the acid may be represented by the following general formula:



Acid (Lactol form)

Phenolic compound.

Dye molecule.

DYES:

(2-hydroxy 5-methyl phenyl) phenol tetra chloro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

(2-hydroxy 5-methyl phenyl) resorcinol tetrachloro phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

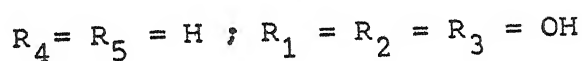
(2-hydroxy 5-methyl phenyl) catechol tetrachloro phthal-as-ein.

$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

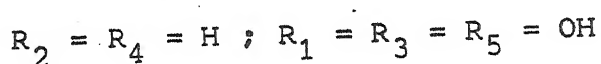
(2-hydroxy 5-methyl phenyl) hydroquinone tetrachloro phthal-as-ein.

$R_2 = R_3 = R_5 = H$; $R_1 = R_4 = OH$

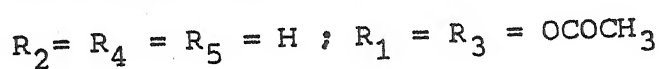
(2-hydroxy 5-methyl phenyl) pyrogallol tetrachloro phthal-as-ein.



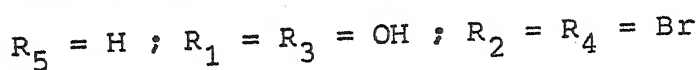
(2-hydroxy 5-methyl phenyl) phloroglucinol tetrachloro phthal-as-ein.



(2-acetoxy 5-methyl phenyl) diacetyl resorcinol tetrachloro phthal-as-ein.



(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol tetrachloro phthal-as-ein.



(2-HYDROXY 5-METHYL PHENYL) PHENOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the homogeneous mixture of the acid (2.0g) and phenol (1.5g) at 160-170°C for about four hours in presence of few drops of concentrated sulphuric acid. The isolation and purification of the dye were done as described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, yield 1.6g.

The reddish orange coloured dye m.p. 220-222°C, dissolves in ethanol giving light yellow colour. The colour becomes violet on addition of alkali.

Anal.for. : $C_{21}H_{12}Cl_4O_4$ (Mol.wt.470)

Calc. : C, 53.62; H, 2.55; Cl, 30.21;

Found : C, 53.54; H, 2.51; Cl, 30.12;

(2-HYDROXY 5-METHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by heating the intimate mixture of the acid (5.0g) and resorcinol (3.0g) in an oil bath at 140-160°C in presence of concentrated sulphuric acid (4-5 drops) for about four hours. The dye was isolated and purified exactly in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 171), yield 4.6g.

The greenish brown coloured dye having m.p. 280-281°C, is soluble in ethanol methanol and acetic acid. Its ethanolic solution gives cream colour, which turns into reddish orange colour with green fluorescence on adding a drop of alkali.

Anal.for. : $C_{21}H_{12}Cl_4O_5$ (Mol.wt. 486)

Calc. : C, 51.85; H, 2.47; Cl, 29.22;

Found : C, 51.76; H, 2.43; Cl, 29.17;

(2-HYDROXY 5-METHYL PHENYL) CATECHOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the homogeneous mixture of the acid (2.5g) and catechol (1.6g) at 120-130°C in presence of 3-4 drops of conc. sulphuric acid. Isolation and purification of the dye were carried out similarly as in case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, yield.

The black coloured dye having m.p. 242-243°C, is soluble in acetone alcohol and acetic acid. Its ethanolic

solution is golden-brown in colour, which turns into brown on addition of alkali.

Anal.for. : $C_{21}H_{12}Cl_4O_5$ (Mol.wt. 486)

Calc. : C, 51.85; H, 2.47; Cl, 29.22;

Found : C, 51.75; H, 2.44; Cl, 29.18;

(2-HYDROXY 5-METHYL PHENYL) HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the homogeneous mixture of acid (2.0g) and hydroquinone (1.0g) at $160-180^{\circ}C$ for about three and half hours in presence of concentrated sulphuric acid (2-3 drops), yield 1.7g.

The black dye decomposed above $270^{\circ}C$, dissolves in ethanol giving light brown colour, which turns into brown on addition of alkali.

Anal.for. : $C_{21}H_{12}Cl_4O_5$ (Mol.wt. 486)

Calc. : C, 51.85; H, 2.47; Cl, 29.22;

Found : C, 51.76; H, 2.43; Cl, 29.16;

(2-HYDROXY 5-METHYL PHENYL) PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

An intimate mixture of the acid (2.0g) and pyrogallol (1.0g) was heated in an oil bath at $130-140^{\circ}C$ for three hours in presence of 2-3 drops of conc. sulphuric acid. The isolation and purification of the dye were done in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 171), yield 1.5g.

The black coloured dye having m.p. above 360°C , is soluble in acetone, alcohol and acetic acid. The ethanolic solution is dark brown in colour. On adding a drop of alkali the colour becomes blue in colour.

Anal.for. : $\text{C}_{21}\text{H}_{12}\text{Cl}_4\text{O}_6$ (Mol.wt. 502)

Calc. : C, 50.20; H, 2.39; Cl, 28.29;

Found : C, 50.11; H, 2.36; Cl, 28.22;

(2-HYDROXY 5-METHYL PHENYL) PHLOROGLUCINOL TETRACHLORO
PHTHAL-AS-EIN :

It was prepared by condensing the intimate mixture of the acid (1.5g) and phloroglucinol (1.0g) at $180-200^{\circ}\text{C}$ for about four hours in presence of few drops (3-5) of concentrated sulphuric acid, yield 1.32g.

The dark red dye m.p. 180°C dissolves in ethanol giving wine red colour. The colour becomes red with green fluorescence on addition to alkali. It is soluble in acetone, ethanol, methanol and in acetic acid.

Anal.for. : $\text{C}_{21}\text{H}_{12}\text{Cl}_4\text{O}_6$ (Mol.wt. 502)

Calc. : C, 50.20; H, 2.39; Cl, 28.29;

Found : C, 50.09; H, 2.35; Cl, 28.23;

ACETYLATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL
TETRACHLORO PHTHAL-AS-EIN :

[(2-acetoxy 5-methyl phenyl) diacetyl resorcinol tetrachloro
phthal-as-ein]

The dye (2-hydroxy 5-methyl phenyl) resorcinol tetra

chloro phthal-as-ein (1.0g) was acetylated, isolated and purified exactly in a similar manner as in the case of acetylation of (4-amino 3-chloro phenyl) tetrachloro resorcinol phthal-as-ein (page 174), yield 0.62g. The golden brown coloured triacetyl derivative having m.p. 165-167°C, is soluble in benzene ether, chloroform and acetic acid.

Anal. for. : $C_{27}H_{18}Cl_4O_8$ or $C_{21}H_9Cl_4O_5(COCH_3)_3$ (Mol. wt. 612)

Calc. : C, 52.94; H, 2.94; Cl, 23.20; acetyl, 21.08;

Found : C, 52.85; H, 2.93; Cl, 23.14; acetyl, 21.03;

BROMINATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL
TETRACHLORO PHTHAL-AS-EIN :

[(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol
tetrachloro phthal-as-ein]

The dye (1.0g) was dissolved in a minimum quantity of glacial acetic acid 10ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130°C for an hour.

The crude brominated dye was finally purified by crystallization from the aqueous ethanol and dried at 80°C in an oven and then in vacuum desiccator, yield 0.88g.

The brownish cream coloured dye has m.p. 315-317°C. It is soluble in benzene, ether, alcohol and in chloroform.

Anal. for. : $C_{21}H_9Cl_4Br_3O_5$ (Mol. wt. 723)

Calc. : Br, 33.20; Found : Br, 33.14;

CAUSTIC POTASH TREATMENT OF (2-HYDROXY 5-METHYL PHENYL)
RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

Caustic potash fusion of the dye (1.5g) was carried out exactly in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 176). Following three residues obtained, were identified.

Identification of Residue (I) :

It was identified as unreacted residual dye on the basis of its colour reactions and confirmed by mixed melting point determination with authentic sample.

Identification of Residue (II) :

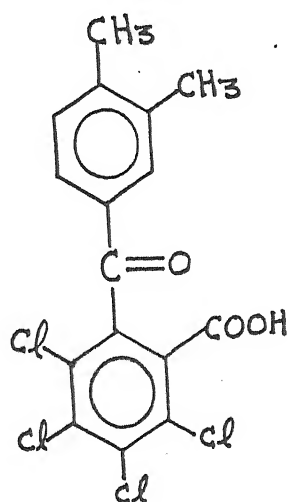
It gave positive tests for carboxyl and phenolic groups and was identified and confirmed as O-(2-hydroxy 5-methyl benzoyl) tetra chloro benzoic acid by mixed melting point determination.

Identification of Residue (III) :

It was identified and confirmed as resorcinol because it gave violet colour with ferric chloride solution, reduced Fehling's solution and Tollen's reagent. It was melted at $109-110^{\circ}\text{C}$. It was further confirmed by mixed melting point determination with the authentic sample.

The acetylation, bromination and caustic potash fusion of the dye are shown in chart C (page 111).

4. DYES DERIVED FROM O-(3,4-DIMETHYL BENZOYL)
TETRACHLORO BENZOIC ACID :



O-(3,4-dimethyl benzoyl)
 tetrachloro benzoic acid.

The acid⁴⁻⁸ was prepared by carrying out Friedel-Crafts reaction between dry AR 80ml of O-xylene and 28.0g of tetrachloro phthalic anhydride in presence of anhydrous aluminium chloride (27.0g) as a catalyst. The yield of the acid obtained was 23.0g. The crude acid was crystallised from methanol in the form of yellow, crystals, m.p. 215-217°C. The acid is soluble in water, ether and methanol.

Anal.for. : $C_{16}H_{10}Cl_4O_3$ (Mol.wt. 392)

Calc. : C, 48.98; H, 2.55; Cl, 36.22;

Found : C, 48.88; H, 2.52; Cl, 36.14;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

It was prepared in a manner similar to that described under acetylation of O-(4-amino 3-chloro benzoyl) tetrachloro

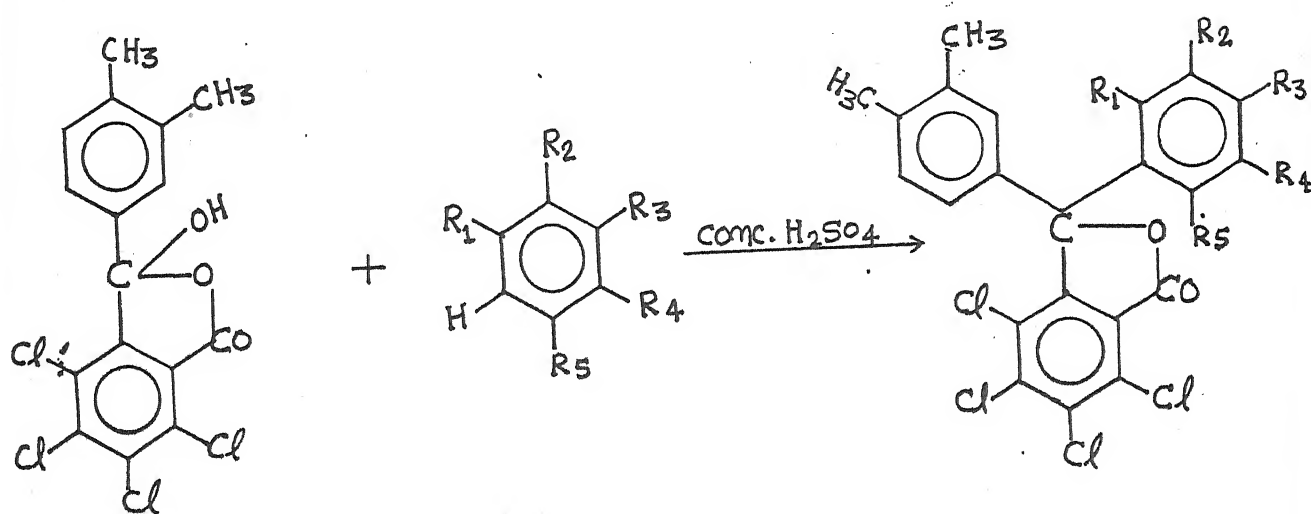
benzoic acid (page 167). The light brown coloured acetylated product soluble in acetone and chloroform has m.p. 120°C .

Anal. for. : $\text{C}_{18}\text{H}_{12}\text{Cl}_4\text{O}_4$ or $\text{C}_{16}\text{H}_9\text{Cl}_4\text{O}_3(\text{COCH}_3)$ (Mol. wt. 434)

Calc. : C, 49.77; H, 2.76; Cl, 32.72; acetyl, 9.91;

Found : C, 49.69; H, 2.72; Cl, 32.65; acetyl, 9.87;

The dyes prepared from the acid may be represented by the following general formula:



Acid (Lactol form)

Phenolic compound.

Dye molecule.

DYES:

(3,4-dimethyl phenyl) phenol tetrachloro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = \text{H} ; R_3 = \text{OH}$

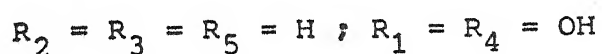
(3,4-dimethyl phenyl) resorcinol tetrachloro phthal-as-ein.

$R_2 = R_4 = R_5 = \text{H} ; R_1 = R_3 = \text{OH}$

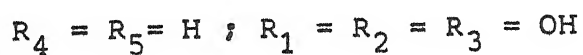
(3,4-dimethyl phenyl) catechol tetrachloro phthal-as-ein.

$R_3 = R_4 = R_5 = \text{H} ; R_1 = R_2 = \text{OH}$

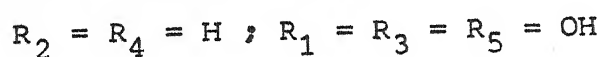
(3,4-dimethyl phenyl) hydroquinone tetrachloro phthal-as-ein.



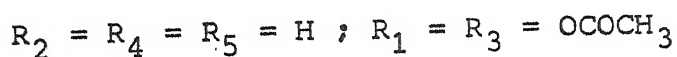
(3,4-dimethyl phenyl) pyrogallol tetrachloro phthal-as-ein.



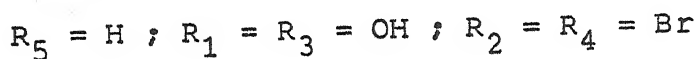
(3,4-dimethyl phenyl) phloroglucinol tetrachloro phthal-as-ein.



(3,4-dimethyl phenyl) diacetyl resorcinol tetrachloro phthal-as-ein.



(3,4-dimethyl phenyl) dibromo resorcinol tetrachloro phthal-as-ein.



(3,4-DIMETHYL PHENYL) PHENOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the homogeneous mixture of the acid (2.0g) and phenol (1.0g) at 160-170°C for four hours in presence of few drops of concentrated sulphuric acid. The dye was isolated and purified similarly as described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, ^{(page 171),} yield 1.82g.

The pink coloured dye has m.p. 232-234°C. Its ethanolic solution is wine red ⁱⁿ _Acoloure which turns into violet on addition of a drop of alkali.

Anal. for. : $C_{22}H_{14}Cl_4O_3$ (Mol. wt. 468)

Calc. : C, 56.41; H, 2.99; Cl, 30.34;

Found : C, 56.32; H, 2.96; Cl, 30.28;

(3,4-DIMETHYL PHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by heating the intimate mixture of the acid (5.2g) and resorcinol (3.0g) in an oil bath at 140-160°C in presence of sulphuric acid (concentrated, 6-8 drops) for about four and half hours. The isolation and purification of the dye were carried out in a manner similar to that described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 171), yield 4.9g.

The golden brown coloured dye, m.p. 281-283°C gives pale creamal colour in ethanol which turns into pinkish orange with green fluorescence on adding a drop of alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal.for. : $C_{22}H_{14}Cl_4O_4$ (Mol.wt. 484)

Calc. : C, 54.55; H, 2.89; Cl, 29.34;

Found : C, 54.44; H, 2.86; Cl, 29.28;

(3,4-DIMETHYL PHENYL) CATECHOL TETRACHLORO PHTHAL-AS-EIN :

Condensation of the acid (2.5g) and catechol (1.5g) was carried out at 120-140°C for four hours by using 3-4 drops of concentrated sulphuric acid as condensing agent. The dye was isolated and purified exactly in a similar manner as the other dyes. The black coloured dye, m.p. 243-245°C gives brown colour in ethanol which is not changed on addition of alkali.

Anal.for. : $C_{22}H_{14}Cl_4O_4$ (Mol.wt. 484)

Calc. : C, 54.55; H, 2.89; Cl, 29.34;

Found : C, 54.45; H, 2.88; Cl, 29.30;

(3,4-DIMETHYL PHENYL) HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

An intimate mixture of the acid (1.5g) and hydroquinone (1.0g) was heated in an oil bath at 160-170°C, in presence of concentrated sulphuric acid (3-4 drops). The reaction, isolation and the purification were carried out in a manner similar to that described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, ^(page 171) yield 1.3g, m.p. 320°C (decomposed).

The light black dye, soluble in ethanol gives golden brown colour which is not changed on adding a drop of alkali. It gives dark brown colour in strong basic medium.

Anal. for. : $C_{22}H_{14}Cl_4O_4$ (Mol. wt. 484)

Calc. : C, 54.55; H, 2.89; Cl, 29.34;

Found : C, 54.46; H, 2.87; Cl, 29.29;

(3,4-DIMETHYL PHENYL) PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (2.0g) and pyrogallol (1.4g) by using 2-3 drops of conc. sulphuric acid as condensing agent. Heating was continued for four hours at 130-145°C, till brittle mass was obtained on cooling. Isolation and purification were done in same way as in case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein, ^(page-171) yield 1.7g.

The blackish brown dye having m.p. above 360°C, is soluble in acetone, ethanol, methanol and acetic acid. It gives golden brown and dark brown colour in ethanol and alcoholic

caustic potash solution respectively.

Anal. for. : $C_{22}H_{14}Cl_4O_5$ (Mol. wt. 500)

Calc. : C, 52.80; H, 2.80; Cl, 28.40;

Found : C, 52.71; H, 2.78; Cl, 28.35;

(3,4-DIMETHYL PHENYL) PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The mixture of acid (2.4g) phloroglucinol (1.6g) and few drops (2-3) of concentrated sulphuric acid, was heated in an oil bath at $190-200^{\circ}C$, for three and half hours. The dye was isolated and purified exactly in a similar manner as the other dyes, yield 3.0g. The dark orange dye having m.p. $240^{\circ}C$ (decomposed), gives wine red colour in ethanol which turns into dark red on adding a drop of alkali.

Anal. for. : $C_{22}H_{14}Cl_4O_5$ (Mol. wt. 500)

Calc. : C, 52.80; H, 2.80; Cl, 28.40;

Found : C, 52.70; H, 2.77; Cl, 28.34;

ACETYLATION OF (3,4-DIMETHYL PHENYL) RESORCINOL
TETRACHLORO PHTHAL-AS-EIN :

[(3,4-dimethyl phenyl) diacetyl resorcinol tetrachloro
phthal-as-ein]

It was carried out in a manner similar to that described under acetylation in (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 174), yield 0.82g.

The buff coloured diacetyl derivative having m.p. $310-312^{\circ}C$, is soluble in benzene, chloroform and acetic acid.

Anal.for. : $C_{26}H_{18}Cl_4O_6$ or $C_{22}H_{12}Cl_4O_4(COCH_3)_2$ (Mol.wt. 568)

Calc. : C, 54.93; H, 3.17; Cl, 25.00; acetyl, 15.14;

Found : C, 54.83; H, 3.13; Cl, 24.93; acetyl, 15.08;

BROMINATION OF (3,4-DIMETHYL PHENYL) RESORCINOL
TETRACHLORO PHTHAL-AS-EIN :

[(3,4-dimethyl phenyl) dibromo resorcinol tetrachloro phthal-as-ein]

The dye (1.0g) was dissolved in a minimum quantity of glacial acetic acid and 10ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of dye. The flask was fitted with an air condenser and the contents were refluxed at $120^{\circ}C$ for an hour. The extraction and purification of the brominated compound were done as in the case of bromination of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 175), yield 0.92g.

The pale yellow coloured dye having m.p. $120-121^{\circ}C$ is soluble in ether, methanol, acetone and chloroform.

Anal.for. : $C_{22}H_{12}O_4Cl_4Br_2$ (Mol.wt. 642)

Calc. : Br, 24.92; Found : Br, 24.85;

CAUSTIC POTASH TREATMENT OF (3,4-DIMETHYL PHENYL)
RESORCINOL TETRACHLORO PHTHAL-AS-EIN :

Caustic potash fusion of the dye (1.0g) was carried out exactly in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol tetrachloro phthal-as-ein (page 176). Finally yielded following three residues:

Identification of Residue (I) :

Residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue (II) :

It was found to be acidic in nature and gave positive test for carboxylic group and was identified as O-(3,4-dimethyl benzoyl) tetra chloro benzoic acid and confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue (III) :

The purified substance (III) melted at 108-110°C. It gave violet blue colour with ferric chloride, reduced Fehling's solution and Tollen's reagent. It responded to fluorescein test with phthalic anhydride on the basis of these observations the residue III was identified as resorcinol. It was further confirmed by mixed melting point determination with the authentic sample.

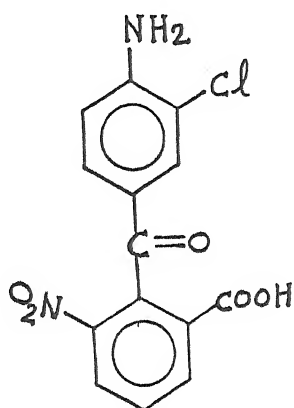
The acetylation, bromination and caustic potash treatment of the dye are shown in chart D (page 114).

CHAPTER - V

This chapter includes the dyes derived from the following acids:-

- (1) O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid.
- (2) O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid.
- (3) O-(3,4-dimethyl benzoyl) m-nitro benzoic acid.

1. DYES DERIVED FROM O-(4-AMINO 3-CHLORO BENZOYL)
m-NITRO BENZOIC ACID :



O-(4-amino 3-chloro benzoyl)
 m-nitro benzoic acid.

The acid⁹⁻¹³ was prepared by carrying out Friedel-Crafts reaction between 2-chloro aniline (85ml, dry AR) and m-nitro phthalic anhydride (20.0g about 0.1 mole) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole) as catalyst. The yield of the acid is 22.5g.

The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried

out below 20°C by adding anhydrous aluminium chloride in portions. When the vigorous reaction subsided, the mixture was heated on boiling water bath until the evolution of hydrogen chloride ceased.

The heavy, dark coloured complex was decomposed by adding 20ml of concentrated hydrochloric acid (in 150ml of, ice cold water). The excess of 2-chloro aniline was removed by steam distillation. The residue was extracted 4-5 times with hot boiling 10% solution of sodium carbonate and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallised from acetone/methanol m.p. $185-187^{\circ}\text{C}$. The light pink crystalline acid is soluble in acetone and methanol.

Anal.for. : $\text{C}_{14}\text{H}_9\text{N}_2\text{ClO}_5$ (Mol.wt. 320.5)

Calc. : C, 52.42; H, 2.81; N, 8.74; Cl, 11.08;

Found : C, 52.34; H, 2.79; N, 8.70; Cl, 11.01;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (1.0g) was acetylated by refluxing it with fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml) at 120°C for four hours. The contents were poured into ice cold water, stirred well and the residue was filtered. It was washed well with cold water and crystallised from dilute acetic acid in the form of light brown crystalline

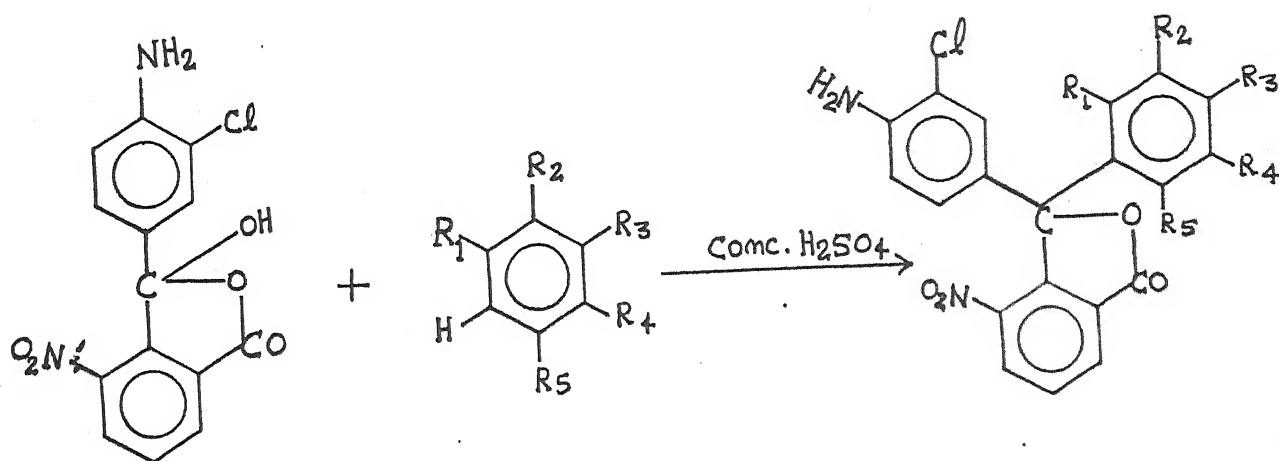
compound, yield 0.75g, m.p.109-110°C. It is soluble in acetone chloroform and acetic acid.

Anal.for. : $C_{18}H_{13}N_2ClO_7$ or $C_{14}H_7N_2ClO_5(COCH_3)_2$ (Mol.wt.404.5)

Calc. : C, 53.40; H, 3.21; N, 6.92; Cl, 8.78; acetyl, 21.26;

Found : C, 53.32; H, 3.18; N, 6.88; Cl, 8.71; acetyl, 21.19;

The dyes prepared from the acid may be represented by the following general formula:



Acid (Lactol form)

Phenolic compound.

Dye molecule.

DYES:

(4-amino 3-chloro phenyl) phenol nitro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

(4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

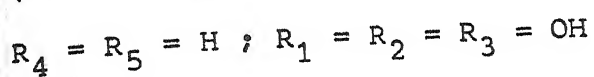
(4-amino 3-chloro phenyl) catechol nitro phthal-as-ein.

$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

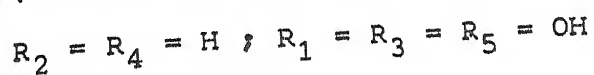
(4-amino 3-chloro phenyl) hydroquinone nitro phthal-as-ein.

$R_2 = R_3 = R_5 = H$; $R_1 = R_4 = OH$

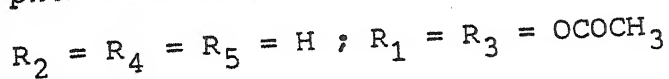
(4-amino 3-chloro phenyl) pyrogallol nitro phthal-as-ein.



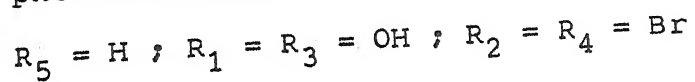
(4-amino 3-chloro phenyl) phloroglucinol nitro phthal-as-ein.



(4-acetyl amino 3-chloro phenyl) diacetyl resorcinol nitro phthal-as-ein.



(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol nitro phthal-as-ein.



(4-AMINO 3-CHLORO PHENYL) PHENOL NITRO PHTHAL-AS-EIN :

The dye was prepared by carrying out the condensation of the acid (3.0g) and phenol (1.5g) slight excess than molecular proportion) was taken in a hard boiling tube and heated in an oil bath at 120°C to make it homogeneous. A few drops of concentrated sulphuric acid were added and the heating was continued at 160-170°C for six hours till the melt become hard and brittle on cooling. The condensed mass was taken out in a flask and subjected to steam distillation to remove excess of phenol. The solid mass left in the flask powdered and extracted with 2% caustic soda solution and filtered. The dye was precipitated from blackish brown coloured filtrate by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum desiccator, yield 2.7g, m.p. 300°C (decomposed).

The blackish brown crystalline dye dissolves in ethanol giving brown colour which turns into reddish violet on adding a drop of alkali.

The purity of the dye was tested by paper chromatography adopting descending technique^{1A,1B}, in a manner similar to described in the case of (4-amino 3-chloro phenyl) phenol tetrachloro phthal-as-ein (Page 170).

Found : Rf (Phenol nitro phthalein), 0.93

Rf (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein,
0.95.

Reported: Rf (Phenol phthalein), 0.92

Anal.for. : $C_{20}H_{13}N_2ClO_5$ (Mol.wt. 396.5)

Calc. : C, 60.53; H, 3.28; N, 7.06, Cl, 8.95;

Found : C, 60.44; H, 3.26; N, 7.02; Cl, 8.91;

(4-AMINO 3-CHLORO PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

An intimate mixture of the acid (5.0g) and resorcinol (3.0g) taken in a 50ml flask, was heated in an oil bath at 140-160°C for four hours in presence of few drops of concentrated sulphuric acid. The dye was isolated and purified exactly in a manner similar to that described in case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein, yield 4.8g.

The greenish brown coloured dye having m.p. 312°C (decomposed) gives lemon yellow colour in ethanol which turns

into red with green fluorescence on adding a drop of alkali.

It is soluble in ethanol, methanol and acetic acid.

Anal.for. : $C_{20}H_{13}N_2ClO_6$ (mol.wt. 412.5)

Calc. : C, 58.18; H, 3.15; N, 6.79; Cl, 8.61;

Found : C, 58.09; H, 3.12; N, 6.74; Cl, 8.56;

(4-AMINO 3-CHLORO PHENYL) CATECHOL NITRO PHTHAL-AS-EIN :

It was prepared by heating the homogeneous mixture of the acid (2.0g) and catechol (1.4g) in an oil bath at 120-130°C for about four hours in presence of concentrated sulphuric acid (2-3 drops). The reaction, isolation and purification were carried out in a similar manner as in case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein, ^(page 206) yield 1.5g, m.p. > 360°C.

! The black coloured dye gives brown colour in ethanol which turns into brownish black on adding a drop of alkali.

Anal.for. : $C_{20}H_{13}N_2ClO_6$ (Mol.wt. 412.5)

Calc. : C, 58.18; H, 3.15; N, 6.79; Cl, 8.61;

Found : C, 58.10; H, 3.13; N, 6.76; Cl, 8.58;

(4-AMINO 3-CHLORO PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the homogeneous mixture of the acid (2.0g) and hydroquinone (1.5g) at 160-180°C for four hours in presence of 2-3 drops of conc. sulphuric acid.

The isolation and purification of the dye were done

in a similar manner as described in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 1.6g.

The black dye decomposed at 234°C gives light brown colour in ethanol. It gives dark brown colour on adding a drop of alkali. It is soluble in alcohol and acetic acid.

Anal.for. : $\text{C}_{20}\text{H}_{13}\text{N}_2\text{ClO}_6$ (Mol.wt. 412.5)

Calc. : C, 58.18; H, 3.15; N, 6.79; Cl, 8.61;

Found : C, 58.08; H, 3.13; N, 6.77; Cl, 8.58;

(4-AMINO 3-CHLORO PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN:

It was prepared by heating the homogeneous mixture of the acid (1.8g) and pyrogallol (1.3g) in an oil bath at $130-140^{\circ}\text{C}$ in presence of concentrated sulphuric acid (2-3 drops) for about four hours. The dye was isolated and purified in a manner similar to that described in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein. (page 206)

The black coloured amorphous dye has m.p. above 360°C . Its ethanolic solution is light brown coloured which turns into brown on addition of a drop of alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal.for. : $\text{C}_{20}\text{H}_{13}\text{N}_2\text{ClO}_7$ (Mol.wt. 428.5)

Calc. : C, 56.01; H, 3.03; N, 6.53; Cl, 8.28;

Found : C, 55.92; H, 3.01; N, 6.49; Cl, 8.22;

(4-AMINO 3-CHLORO PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the mixture of the acid (2.0g) and phloroglucinol (1.5g) at 190-210°C for about four hours in presence of 4-5 drops of conc. sulphuric acid. The reaction, isolation and purification of the dye were carried out in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein, yield 2.56g.

The brownish red dye decomposed at 320°C, gives orange red colour in ethanol. It gives dark orangish red colour on adding a drop of alkali. It is soluble in benzene, acetone, methanol and acetic acid.

Anal.for. : $C_{20}H_{13}N_2ClO_7$ (mol.wt. 428.5)

Calc. : C, 56.01; H, 3.03; N, 6.53; Cl, 8.28;

Found : C, 55.93; H, 3.00; N, 6.48; Cl, 8.24;

ACETYLATION OF (4-AMINO 3-CHLORO PHENYL)
RESORCINOL NITRO PHTHAL-AS-EIN :

[(4-acetamide 3-chloro phenyl) diacetyl resorcinol nitro phthal-as-ein]

The dye (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein (1.0g) and fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml) were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed in an oil bath at 120°C for about four and half hours. The hot contents were then poured slowly into a beaker containing a slush of ice and water with constant

stirring. It was left overnight where upon a brown solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallised from methanol. It was dried in an oven at 80°C and then over phosphorous pentaoxide under reduced pressure, yield 0.65g.

The acetylated product is pale cream in colour, m.p. 280°C . It is soluble in acetone, methanol and acetic acid.

Anal.for. : $\text{C}_{26}\text{H}_{19}\text{N}_2\text{ClO}_9$ (Mol.wt. 538.5)

or $\text{C}_{20}\text{H}_{10}\text{N}_2\text{ClO}_6(\text{COCH}_3)_3$

Calc. : C, 57.94; H, 3.53; N, 5.20; Cl, 6.59; acetyl, 23.96;

Found : C, 57.85; H, 3.49; N, 5.16; Cl, 6.56; acetyl, 23.89;

BROMINATION OF (4-AMINO 3-CHLORO PHENYL)
RESORCINOL NITRO PHTHAL-AS-EIN :

[4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol
nitro phthal-as-ein]

The dye (1.0g) was dissolved in a minimum quantity of glacial acetic 10ml of 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120°C for an hour. Contents were cooled and diluted with minimum quantity of distilled water. A dark brown powder settled. It was filtered and washed well with water containing acetic acid and finally with hot water to remove excess of bromine. It was dissolved in dilute aqueous caustic soda solution and filtered. The filtrate gave bromo derivative of the dye on gradual addition of dilute hydro chloric acid. The

crude brominated dye was finally purified by crystallisation from aqueous ethanol, and dried at 80°C in an oven and then in vacuum desiccator, yield 0.62g.

The dark brown micro crystalline dye, m.p. 182°C (decomposed), dissolves in ether, ethanol, methanol, chloroform and acetic acid.

Anal.for. : $C_{20}H_{10}N_2ClBr_3O_6$ (Mol.wt. 649.5)

Calc. : Br, 36.95; Found : Br, 36.89;

CAUSTIC POTASH TREATMENT OF (4-AMINO 3-CHLORO PHENYL)
RESORCINOL NITRO PHTHAL-AS-EIN :

Caustic potash pellets (5.0g) were heated in a crucible with a few drops of water in order to make it a paste, then the resorcinol dye (1.0g) was added to it. The temperature was raised and heating was continued between 280-300°C, on a sand bath for about four hours until the colour of the dye faded completely. The contents of the crucible were dissolved in 50ml of distilled water and filtered. The dark red residue (I) settled down on just neutralising the excess of alkali. It was filtered and washed well with water. The filtrate on further acidification with excess of dilute hydrochloric acid, gave brownish pink precipitate (II) which was filtered and washed with water. It was crystallised from solvent ether and dried in a vacuum desiccator. The filtrate was shaken with benzene and on evaporation of the excess of the solvent a brown residue (III) was obtained.

Identification of Residue (I) :

Residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue (II) :

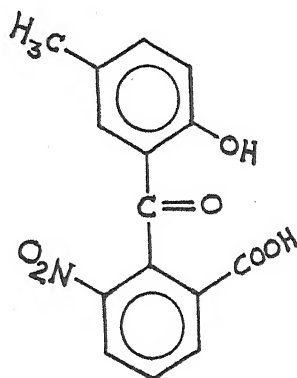
It was found to be acedic and gave positive test for carboxyl, amino and nitro groups. It was identified to be O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid and confirmed by mixed melting point determination (m.p. 185-187°C) and superimposition of the IR spectra with the authentic sample.

Identification of Residue (III) :

The compound, m.p. 110°C, gave violet blue colour with ferric chloride and responded to fluorscein test with phthalic anhydride. It reduced Fehling's solution and ammonical silver nitrate solution. The melting point did not show any depression when mixed with the authentic sample of resorcinol. It was inferred to be resorcinol.

The caustic potash fusion, acetylation and bromination of the resorcinol dye are given in chart A (page 105).

2. DYES DERIVED FROM O-(2-HYDROXY 5-METHYL BENZOYL)
m-NITRO BENZOIC ACID :



O-(2-hydroxy 5-methyl benzoyl)
m-nitro benzoic acid.

The acid⁹⁻¹³ was prepared by carrying out Friedel-Crafts reaction between m-nitro phthalic anhydride (20g about 0.1 mole) and p-cresol (dry AR 100ml) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole), yield 20g. The acid was crystallised from acetone in the form of brown crystals. The acid dissolves in ethanol, methanol and acetone, m.p. 162-164°C.

Anal. for. : $C_{15}H_{11}NO_6$ (Mol. wt. 301.0)

Calc. : C, 59.80; H, 3.65; N, 4.65;

Found : C, 59.72; H, 3.62; N, 4.60;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The acid (1.0g) was acetylated in a same way as in case of acetylation of O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid (page 203). The brownish black acetyl derivative was treated with animal charcoal and finally crystallised from

aqueous ethanol in presence of a drop of acetic acid, yield 0.85g.

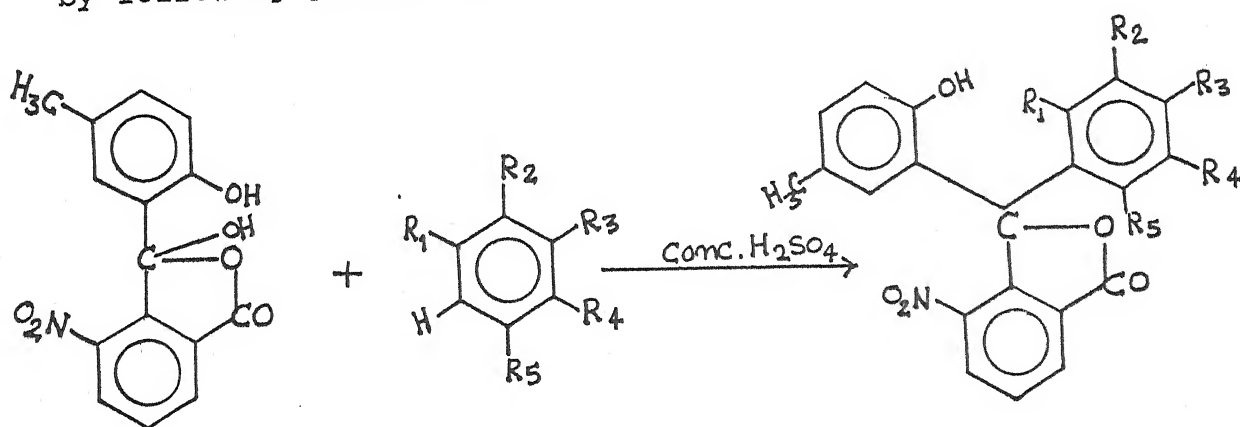
The brown coloured diacetyl derivative having m.p. 135-137°C, is soluble in ethanol, methanol, chloroform and acetic acid.

Anal.for. : $C_{19}H_{15}NO_8$ or $C_{15}H_9NO_6(COCH_3)_2$ (Mol.wt. 385)

Calc. : C, 59.22; H, 3.90; N, 3.64; acetyl, 22.34;

Found : C, 59.14; H, 3.86; N, 3.61; acetyl, 22.26;

The dyes prepared from the acid may be represented by following general formula:



Acid (Lactol form)

Phenolic compound.

Dye molecule.

DYES:

(2-hydroxy 5-methyl phenyl) phenol nitro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

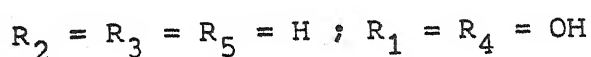
(2-hydroxy 5-methyl phenyl) resorcinol nitro phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

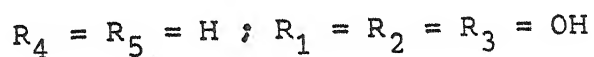
(2-hydroxy 5-methyl phenyl) catechol nitro phthal-as-ein.

$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

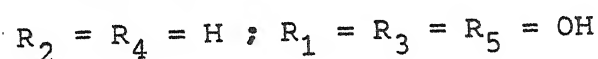
(2-hydroxy 5-methyl phenyl) hydroquinone nitro phthal-as-ein.



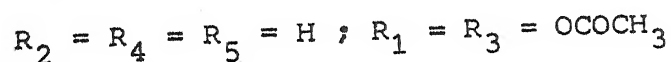
(2-hydroxy 5-methyl phenyl) pyrogallol nitro phthal-as-ein.



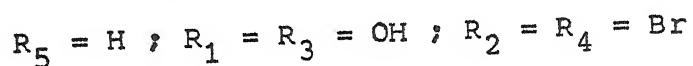
(2-hydroxy 5-methyl phenyl) phloroglucinol nitro phthal-as-ein.



(2-acetoxy 5-methyl phenyl) diacetyl resorcinol nitro phthal-as-ein.



(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol nitro phthal-as-ein.



(2-HYDROXY 5-METHYL PHENYL) PHENOL NITRO PHTHAL-AS-EIN :

The dye was prepared by heating the intimate mixture of the acid (2.5g) and phenol (2.0g) in an oil bath at 160-175°C for about four hours in presence of 3-5 drops of concentrated sulphuric acid. The dye was isolated and purified exactly in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 2.3g.

The brown dye is micro crystalline in nature, m.p. >360°C. It is soluble in ethanol, methanol and acetone. Its ethanolic solution is light brown and on addition of a drop of alkali becomes light pink.

Anal.for. : $C_{21}H_{15}NO_6$ (Mol.wt. 377)

Calc. : C, 66.84; H, 3.98; N, 3.71;

Found : C, 66.75; H, 3.96; N, 3.69;

(2-HYDROXY 5-METHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN :

It was prepared by heating the homogeneous mixture of the acid (5.0g) and resorcinol (3.0g) in an oil bath at $140-160^{\circ}C$ for about four hours, in presence of 4-5 drops of conc.sulphuric acid. The dye was isolated and purified exactly in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 4.6g.

The brown coloured dye having m.p. $301-303^{\circ}C$ is soluble in acetone ethanol, methanol and acetic acid. Its ethanolic solution is light yellow which turns into brownish red with green fluorescence on adding a drop of alkali.

Anal.for. : $C_{21}H_{15}NO_7$ (Mol.wt. 393)

Calc. : C, 64.12; H, 3.82; N, 3.56;

Found : C, 64.03; H, 3.79; N, 3.52;

(2-HYDROXY 5-METHYL PHENYL) CATECHOL NITRO PHTHAL-AS-EIN:

The dye was prepared isolated and purified identically as described in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206). Acid (2.5g) and catechol (1.5g) and few drops (2-3) of conc.sulphuric acid were heated at $120-130^{\circ}C$ for three hours, yield 2.1g.

The brownish black dye having m.p. $>360^{\circ}\text{C}$ gives light brown colour with ethanol. It gives brown colour on adding a drop of alkali.

Anal.for. : $\text{C}_{21}\text{H}_{15}\text{NO}_7$ (Mol.wt. 393)

Calc. : C, 64.12; H, 3.82; N, 3.56;

Found : C, 64.01; H, 3.78; N, 3.51;

(2-HYDROXY 5-METHYL PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN:

The dye was prepared by carrying out the condensation of the acid (1.5g) and hydroquinone (1.0g) in an oil bath at $160-180^{\circ}\text{C}$ for three hours in presence of 2-3 drops of concentrated sulphuric acid. The dye was isolated and purified in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein, yield 1.2g.

The black coloured dye, m.p. 262°C (decomposed), gives light brown colour in ethanol which turns into brown on adding a drop of alkali.

Anal.for. : $\text{C}_{21}\text{H}_{15}\text{NO}_7$ (Mol.wt. 393)

Calc. : C, 64.12; H, 3.82; N, 3.56;

Found : C, 63.97; H, 3.80; N, 3.53;

(2-HYDROXY 5-METHYL PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN:

The dye is prepared by heating the homogeneous mixture of the acid (1.5g) and pyrogallol (1.0g) at $130-140^{\circ}\text{C}$ on an oil bath for three hours in presence of few drops of concentrated

sulphuric acid. The dye was isolated and purified similarly as described in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 1.3g.

The brownish black dye having m.p. $>360^{\circ}\text{C}$, dissolves in ethanol giving light brown colour, which darkens on adding a drop of alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal.for. : $\text{C}_{21}\text{H}_{15}\text{NO}_8$ (Mol.wt. 409)

Calc. : C, 61.61; H, 3.67; N, 3.42;

Found : C, 61.53; H, 3.53; N, 3.40;

(2-HYDROXY 5-METHYL PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The condensation of the intimate mixture of acid (2.5g) and phloroglucinol (1.6g) was carried out in presence of few drops (3-4) of conc. sulphuric acid at $190-200^{\circ}\text{C}$ for about three hours. Isolation and purification of the dye were done as in the case of other dyes, yield 1.9g.

The red dye having m.p. $>360^{\circ}\text{C}$, gives wine red colour with ethanol, which turns into orange red on adding a drop of alkali. It is soluble in benzene, alcohol, acetone and acetic acid.

Anal.for. : $\text{C}_{21}\text{H}_{15}\text{NO}_8$ (Mol.wt. 409)

Calc. : C, 61.61; H, 3.67; N, 3.42;

Found : C, 61.52; H, 3.64; N, 3.39;

ACETYLATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL
NITRO PHTHAL-AS-EIN :

[(2-acetoxy 5-methyl phenyl) diacetyl resorcinol nitro
phthal-as-ein]

The dye (2-hydroxy 5-methyl phenyl) resorcinol nitro phthal-as-ein, 1.0g, was acetylated, isolated and purified exactly in a similar manner as in acetylation of (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein (page 210), yield 0.8g. The light yellow coloured triacetyl derivative having m.p. 242°C , is soluble in acetone alcohol and acetic acid.

Anal.for. : $\text{C}_{27}\text{H}_{21}\text{NO}_{10}$ or $\text{C}_{21}\text{H}_{12}\text{NO}_7(\text{COCH}_3)_3$ (Mol.wt.519)

Calc. : C, 62.43; H, 4.05; N, 2.70; acetyl, 24.86;

Found : C, 62.33; H, 4.01; N, 2.68; acetyl, 24.80;

BROMINATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL
NITRO PHTHAL-AS-EIN :

[(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol
nitro phthal-as-ein]

The dye (1.2g) was brominated, isolated and purified exactly in a same manner as in case of bromination of (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein (Page 211), yield 0.90g.

The brown coloured dye having m.p. 174°C , is soluble in solvent ether, ethanol, methanol, acetone, chloroform and acetic acid.

Anal.for. : $C_{21}H_{12}NO_7Br_3$ (Mol.wt. 630)

Calc. : Br, 38.10; Found : Br, 38.02;

CAUSTIC POTASH TREATMENT OF (2-HYDROXY 5-METHYL PHENYL)
RESORCINOL NITRO PHTHAL-AS-EIN :

Caustic potash fusion of the dye (1.0g) was carried out exactly in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein (page 212). As a result following three residues were obtained.

Identification of Residue (I) :

Residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue (II) :

It gave positive test for carboxyl and phenolic groups which was identified and confirmed as O-(2-hydroxy 5-methyl benzoyl) m-nitro benzoic acid by mixed melting point determination and superimposition of IR spectra with the authentic sample.

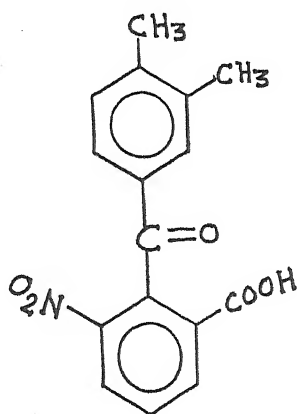
Identification of Residue (III) :

It was identified and confirmed as resorcinol because it gave violet colour with ferric chloride solution, reduced Fehling's solution and Tollen's reagent. It melted at $110^{\circ}C$. It was further confirmed by mixed melting point determination

with the authentic sample

The acetylation, bromination and caustic potash fusion of the dye are shown in chart C (page 111).

3. DYES DERIVED FROM O-(3,4-DIMETHYL BENZOYL)m-NITRO BENZOIC ACID:



[O-(3,4-dimethyl benzoyl)
m-nitro benzoic acid.]

The acid⁹⁻¹³ was prepared by carrying out Friedel-Crafts reaction between m-nitro phthalic anhydride (20.0g about 0.1 mole) and O-xylene (dry AR 80ml) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole), yield 21.0g. The acid was crystallised from acetone in the form of white crystals. The acid dissolves in ethanol, methanol and acetone, m.p. 127-129°C.

Anal.for. : $C_{16}H_{13}NO_5$ (Mol.wt. 299)

Calc. : C, 64.21; H, 4.35; N, 4.68;

Found : C, 64.11; H, 4.32; N, 4.65;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acid (1.0g) was acetylated in a same way as in case of acetylation of O-(4-amino 3-chloro benzoyl) m-nitro benzoic acid (page 204). The brown acetyl derivative was treated

with animal charcoal and finally crystallised from aqueous ethanol in presence of a drop of acetic acid, yield 0.82g.

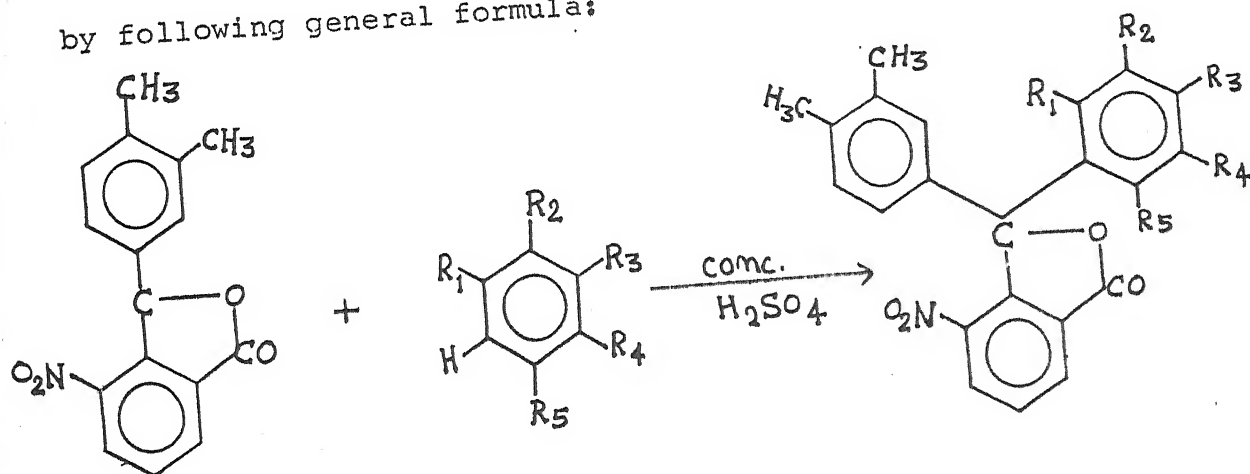
The brown coloured acetyl derivative having m.p. 117-118°C, is soluble in acetone, chloroform and acetic acid.

Anal.for.: $C_{18}H_{15}NO_6$ or $C_{16}H_{12}NO_5(COCH_3)$ (Mol.wt. 341)

Calc. : C, 63.34; H, 4.40; N, 4.11; acetyl, 12.61;

Found : C, 63.26; H, 4.36; N, 4.09; acetyl, 12.54;

The dyes prepared from the acid may be represented by following general formula:



Acid (Lactol form)

Phenolic compound.

Dye molecule.

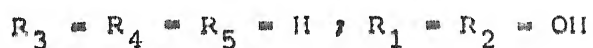
(3,4-dimethyl phenyl) phenol nitro phthal-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

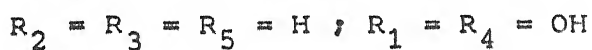
(3,4-dimethyl phenyl) resorcinol nitro phthal-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

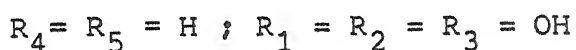
(3,4-dimethyl phenyl) catechol nitro phthal-as-ein.



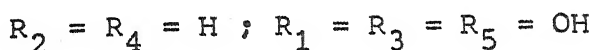
(3,4-dimethyl phenyl) hydroquinone nitro phthal-as-ein.



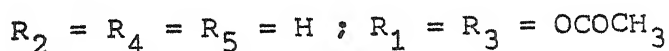
(3,4-dimethyl phenyl) pyrogallol nitro phthal-as-ein.



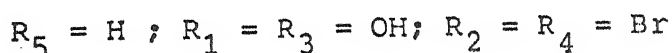
(3,4-dimethyl phenyl) phloroglucinol nitro phthal-as-ein.



(3,4-dimethyl phenyl) diacetyl resorcinol nitro phthal-as-ein.



(3,4-dimethyl phenyl) dibromo resorcinol nitro phthal-as-ein.



(3,4-DIMETHYL PHENYL) PHENOL NITRO PHTHAL-AS-EIN:

An intimate mixture of the acid (1.5g) and phenol (1.0g) was condensed in an oil bath in presence of conc. sulphuric acid (2-3 drops) at 160-170°C for about four hours in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 1.1g.

The light brown micro crystalline dye, m.p. above 360°C, is soluble in acetone, alcohol and acetic acid. Its ethanolic solution is light brown which turns into light violet on adding a drop of alkali.

Anal.for. : $C_{22}H_{17}NO_5$ (Mol.wt. 375)

Calc. : C, 70.40; H, 4.53; N, 3.73;

Found : C, 70.29; H, 4.51; N, 3.69;

(3,4-DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the intimate mixture of acid (5.1g) and resorcinol (3.1g) on the oil bath in presence of few drops (5-6) of conc.sulphuric acid at 140-150°C for about four hours. The isolation and purification were carried out in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 5.2g.

The brown crystalline dye having m.p.284-286°C, is soluble in ethanol, methanol, acetone and acetic acid. Its ethanolic solution is brown in colour which turns into brownish red with green fluorescence on addition of alkali.

Anal.for. : $C_{22}H_{17}NO_6$ (Mol.wt. 391)

Calc. : C, 67.52; H, 4.35; N, 3.58;

Found : C, 67.44; H, 4.29; N, 3.55;

(3,4-DIMETHYL PHENYL) CATECHOL NITRO PHTHAL-AS-EIN:

The dye was prepared by heating the homogenous mixture of the acid (2.0g) and catechol (1.5g) in an oil bath at 120-130°C for about three and half hours in presence of 3-4 drops of conc.sulphuric acid. The isolation and purification of

the dye were done as in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 1.6g.

The black dye having m.p. above 360°C , is soluble in ethanol, methanol and acetic acid. Its ethanolic solution is brown in colour which turns into blackish-brown on adding a drop of alkali.

Anal.for. : $\text{C}_{22}\text{H}_{17}\text{NO}_6$ (Mol.wt. 391)
 Calc. : C, 67.52; H, 4.35; N, 3.58;
 Found : C, 67.47; H, 4.32; N, 3.53;

(3,4-DIMETHYL PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN:

The dye was prepared identically as described in the case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206). Acid (2.5g), hydroquinone (1.5g), and 2-3 drops of conc. sulphuric acid were heated at $160-180^{\circ}\text{C}$ for four hours, yield 2.6g.

The black dye having m.p. 210°C (decomposed), is soluble in ethanol, methanol and acetic acid. Its ethanolic solution is light brown which becomes dark on addition of alkali.

Anal.for. : $\text{C}_{22}\text{H}_{17}\text{NO}_6$ (Mol.wt. 391)
 Calc. : C, 67.52; H, 4.35; N, 3.58;
 Found : C, 67.42; H, 4.30; N, 3.56;

(3,4-DIMETHYL PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN:

The mixture of acid (2.5g), pyrogallol (1.6g) and 3-4 drops of conc.sulphuric acid, was heated in an oil bath at 130-140°C for about four hours. The isolation and purification of the dye were carried out in a similar manner as in case of (4-amino 3-chloro phenyl) phenol nitro phthal-as-ein (page 206), yield 3.1g.

The black crystalline dye having m.p. above 360°C, is soluble in alcohol, acetone and acetic acid. Its ethanolic solution is light brown which turn into brown on adding a drop of alkali.

Anal.for. : $C_{22}H_{17}NO_7$ (Mol.wt. 407)

Calc. : C, 64.86; H, 4.18; N, 3.44;

Found : C, 64.78; H, 4.14; N, 3.41;

(3,4-DIMETHYL PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

It was prepared by heating the homogeneous mixture of the acid (2.5g), phloroglucinol (1.6g) and 3-4 drops of conc.sulphuric acid in an oil bath at 190-200°C for about four hours. The dye was isolated and purified exactly in a similar manner as the other dyes.

The brownish red dye decomposed at 339-340°C. It is soluble in benzene, ethanol, acetone and acetic acid. Its ethanolic solution is brown in colour which turns into red on adding

a drop of alkali.

Anal.for. : $C_{22}H_{17}NO_7$ (Mol.wt. 407)

Calc. : C, 64.86; H, 4.18; N, 3.44;

Found : C, 64.76; H, 4.15; N, 3.40;

ACETYLATION OF (3,4-DIMETHYL PHENYL) RESORCINOL
NITRO PHTHAL-AS-EIN :

[(3,4-dimethyl phenyl) diacetyl resorcinol nitro phthal-as-ein]

Starting with (1.0g) of the dye (3.0g) of fused sodium acetate and 15ml of acetic anhydride, the acetyl derivative was prepared exactly in a similar manner as in the case of other keto acids. The reddish yellow acetyl derivative was treated with animal charcoal and finally crystallised from aqueous ethanol in presence of a drop of acetic acid, yield 0.74g.

The yellow coloured diacetyl derivative decomposed at $235-236^{\circ}C$, is soluble in alcohol, acetone and acetic acid.

Anal.for. : $C_{26}H_{21}NO_8$ or $C_{22}H_{15}NO_6(COCH_3)_2$ (Mol.wt. 475)

Calc. : C, 65.68; H, 4.42; N, 2.95; acetyl, 18.11;

Found : C, 65.58; H, 4.38; N, 2.92; acetyl, 18.06;

BROMINATION OF (3,4-DIMETHYL PHENYL) RESORCINOL
NITRO PHTHAL-AS-EIN :

[(3,4-dimethyl phenyl) dibromo resorcinol nitro phthal-as-ein]

The dye (3,4-dimethyl phenyl)resorcinol nitro phthal-as-ein (1.0g) was brominated exactly in a similar manner as described in the case of (4-amino 3-chloro phenyl) resorcinol

(page 211)
nitro phthal-as-ein, yield 0.92g.

The dark brown micro crystalline dye decomposed at 212-213°C, is soluble in ether, alcohol, acetone, chloroform and acetic acid.

Anal.for. : $C_{22}H_{15}NO_6Br_2$ (Mol.wt. 549)

Calc. : Br, 29.14; Found : Br, 29.08;

CAUSTIC POTASH TREATMENT OF (3,4-DIMETHYL PHENYL)
RESORCINOL NITRO PHTHAL-AS-EIN :

Caustic potash fusion of the dye (1.0g) was carried out similarly as the method described in the case of (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein (page) following three residues obtained were identified.

Identification of Residue (I) :

It was identified as the unreacted residual dye, giving all colour reactions of the dye itself and was further confirmed by mixed melting point determination with original dye.

Identification of Residue (II) :

It was recrystallised from acetone m.p. 127-129°C. It gave positive tests for carboxyl and nitro groups and was confirmed to be O-(3,4-dimethyl benzoyl) m-nitro benzoic acid from mixed melting point determination with the authentic sample, which shows no depression in melting point.

Identification of Residue (III) :

It was identified and confirmed as resorcinol from its colour reactions and mixed melting point determination with the authentic sample.

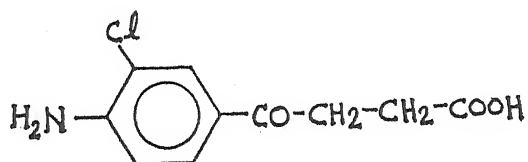
Caustic potash fusion, acetylation and bromination of resorcinol dye, are shown in chart D (page 114).

CHAPTER - VI

The chapter VI includes the dyes derived from following acids:-

- (1) β -(4-amino 3-chloro benzoyl) propionic acid.
- (2) β -(2-hydroxy 5-methyl benzoyl) propionic acid.
- (3) β -(3,4-dimethyl benzoyl) propionic acid.

1. DYES DERIVED FROM β -(4-AMINO 3-CHLORO BENZOYL) PROPIONIC ACID:



[β -(4-amino 3-chloro benzoyl) propionic acid]

The acid was prepared by carrying out Friedel-Crafts reaction between succinic anhydride (10.0g about 0.1 mole) and 2-chloro aniline (dry AR 75ml) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole) as catalyst. The yield of the acid was 16.8g.

The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 25°C by adding anhydrous aluminium chloride in portions. When the vigorous reaction subsided, the mixture was heated on boiling water bath until the evolution of hydrogen chloride ceased.

The heavy, dark brown coloured complex was decomposed by adding 25ml of conc. hydrochloric acid (in 250ml ice cold water). The excess of 2-chloro aniline was removed by steam distillation. The residue was extracted 3-4 times with hot boiling 10% solution of sodium carbonate and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water dried and crystallised from benzene/petroleum ether, m.p. 122-124°C. The white crystalline acid is soluble in benzene, ether and methanol.

Anal. for. : $C_{10}H_{10}NClO_3$ (Mol. wt. 227.5)

Calc. : C, 52.75; H, 4.40; N, 6.15; Cl, 15.60;

Found : C, 52.66; H, 4.36; N, 6.10; Cl, 15.52;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

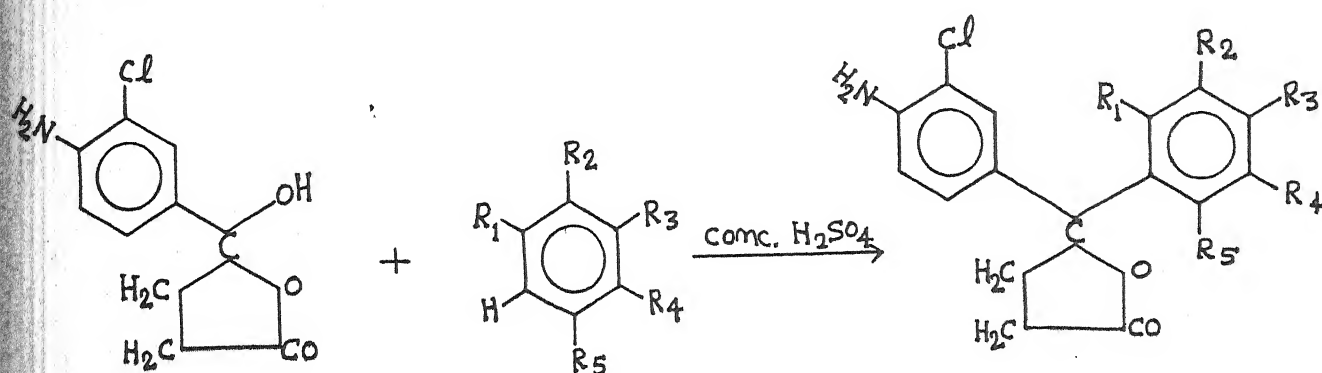
The acid (1.0g) and fused sodium acetate (3.0g) were refluxed with 15ml of freshly distilled acetic anhydride at 130-135°C for three and half hours. The hot contents were poured in a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of coloured solid mass. The brown acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was finally crystallised from acetone, yield 0.72g, m.p. 118°C. It is soluble in acetone, chloroform and acetic acid.

Anal. for. : $C_{14}H_{14}NClO_5$ or $C_{10}H_8NClO_3(COCH_3)_2$ (Mol. wt. 311.5)

Calc. : C, 53.93; H, 4.49; N, 4.49; Cl, 11.40; acetyl, 27.61;

Found : C, 53.82; H, 4.45; N, 4.46; Cl, 11.34; acetyl, 27.53;

The dyes prepared from the acid may be represented by the following structures:



Acid (Lactol form) Phenolic compound. Dye molecule.

(4-amino 3-chloro phenyl) phenol succin-as-ein.

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H} ; \text{R}_3 = \text{OH}$

(4-amino 3-chloro phenyl) resorcinol succin-as-ein.

$\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H} ; \text{R}_1 = \text{R}_3 = \text{OH}$

(4-amino 3-chloro phenyl) catechol succin-as-ein.

$\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{H} ; \text{R}_1 = \text{R}_2 = \text{OH}$

(4-amino 3-chloro phenyl) hydroquinone succin-as-ein.

$\text{R}_2 = \text{R}_3 = \text{R}_5 = \text{H} ; \text{R}_1 = \text{R}_4 = \text{OH}$

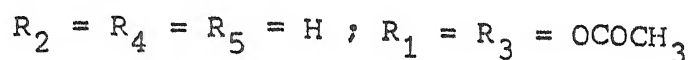
(4-amino 3-chloro phenyl) pyrogallol succin-as-ein.

$\text{R}_4 = \text{R}_5 = \text{H} ; \text{R}_1 = \text{R}_2 = \text{R}_3 = \text{OH}$

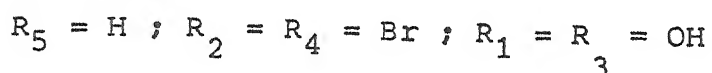
(4-amino 3-chloro phenyl) phloroglucinol succin-as-ein.

$\text{R}_2 = \text{R}_4 = \text{H} ; \text{R}_1 = \text{R}_3 = \text{R}_5 = \text{OH}$

(4-acetyl amino 3-chloro phenyl) diacetyl resorcinol succin-
-as-ein.



(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol succin-
-as-ein.



(4-AMINO 3-CHLORO PHENYL) PHENOL SUCCIN-AS-EIN :

A well ground mixture of the acid (2.5g) and (1.5g) of phenol (slight excess than the molecular proportion) was taken in a hard boiling tube and heated in an oil bath to make the contents homogeneous, few drops of conc. sulphuric acid were then added and heating was continued at 160-170°C for four hours till the molten mass of the tube become brittle on cooling. The condensed mass was taken out from the tube and subjected to steam distillation to remove excess of phenol. The brown solid mass left in the flask was powdered and extracted with 2% sodium hydroxide solution. It was filtered and the dye was precipitated from the coloured filtrate by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum desiccator, yield 2.2g, m.p. 110-111°C.

The brown dye is soluble in ethanol acetone and acetic acid. The purity of the dye was tested by paper chromatography adopting technique^{1A, 1B}.

Paper	Whatman No.1
Mobile phase	Butanol saturated with Ammonia.
Developing agent	1% aqueous caustic soda
Reference dye	Phenolphthalein.

A 25x10 cm strip was taken and a very dilute ethanolic solution of the dye was spotted on the paper (on a base line, 4Cm from one end) with a micro syringe. Similarly a dilute aqueous solution of reference dye was also spotted on the base line at a distance of about 3Cm from the former spot. The mobil phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed with 1% aqueous alkaline solution. After drying the sprayed chromatogram, each dye gave only one corresponding pink spot. This confirmed the homogeneity and purity of (4-amino 3-chloro phenyl) phenol succin-as-ein dye.

Found : Rf (Phenolphthalein), 0.93
 Rf (4-amino 3-chloro phenyl) phenol succin-as-ein,
 0.95

Reported : Rf (Phenolphthalein), 0.92

Anal.for. : $C_{16}H_{14}NClO_3$ (Mol.wt. 303.5)

Calc. : C, 63.26; H, 4.61; N, 4.61; Cl, 11.70;

Found : C, 63.15; H, 4.58; N, 4.57; Cl, 11.63;

(4-AMINO 3-CHLORO PHENYL) RESORCINOL SUCCIN-AS-EIN:

An intimate mixture of acid (5.0g) and resorcinol

(2.6g) was heated in an oil bath at 140-150°C for four hours, in presence of few (5-7) drops of conc.sulphuric acid. The isolation and purification of the dye were done in a similar manner as described in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 5.0g.

The orange dye having m.p. 207-209°C, dissolves in ethanol giving wine red colour. The colour becomes reddish orange with green fluorescence on addition of alkali. It is soluble in ethanol, methanol, acetone and acetic acid.

Anal.for. : $C_{16}H_{14}NClO_4$ (Mol.wt. 319.5)

Calc. : C, 60.09; H, 4.38; N, 4.38; Cl, 11.11;

Found : C, 59.98; H, 4.35; N, 4.36; Cl, 11.06;

(4-AMINO 3-CHLORO PHENYL) CATECHOL SUCCIN-AS-EIN :

The dye was prepared by heating the intimate mixture of acid (2.5g), catechol (1.5g) and 2-3 drops of conc.sulphuric acid at 120-130°C for about four hours. The dye was isolated and purified exactly in the same way as in the (4-amino 3-chloro phenyl) phenol succin-as-ein, yield 1.9g.

The black crystalline dye having m.p. above 360°C, is soluble in alcohol and acetic acid. Its ethanolic solution is light brown which turns into brown on adding a drop of alkali.

Anal.for. : $C_{16}H_{14}NClO_4$ (Mol.wt. 319.5)

Calc. : C, 60.09; H, 4.38; N, 4.38; Cl, 11.11;

Found : C, 60.00; H, 4.34; N, 4.36; Cl, 11.07;

(4-AMINO 3-CHLORO PHENYL) HYDROQUINONE SUCCIN-AS-EIN:

The dye was prepared by carrying out condensation of the acid (2.4g) and hydroquinone (1.5g) at 160-180°C for three hours in presence of 2-4 drops of concentrated sulphuric acid. The isolation and purification were done in a similar manner as described in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 2.0g.

The brown coloured dye decomposed at 250°C. Its ethanolic solution is light brown which turns into dark on addition of 2% alkali.

Anal.for. : $C_{16}H_{14}NClO_4$ (Mol.wt. 319.5)

Calc. : C, 60.09; H, 4.38; N, 4.38; Cl, 11.11;

Found : C, 59.99; H, 4.35; N, 4.36; Cl, 11.06;

(4-AMINO 3-CHLORO PHENYL) PYROGALLOL SUCCIN-AS-EIN:

It was prepared by condensing the homogeneous mixture of the acid (2.5g) pyrogallol (1.5g) and 3-5 drops of concentrated sulphuric acid at 130-140°C for three hours. The dye was isolated and purified similarly as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 3.0g.

The brown dye having m.p. above 360°C, is soluble in ethanol, methanol, acetone and acetic acid. Its ethanolic solution is light brown. The colour becomes deep on adding a drop of alkali.

Anal.for. : $C_{16}H_{14}NClO_5$ (Mol.wt. 335.5)

Calc. : C, 57.23; H, 4.17; N, 4.17; Cl, 10.58;

Found : C, 57.14; H, 4.15; N, 4.13; Cl, 10.54;

(4-AMINO 3-CHLORO PHENYL) PHLOROGLUCINOL SUCCIN-AS-EIN:

The dye was prepared by carrying out the condensation of the acid (2.0g) and phloroglucinol (1.3g) in an oil bath at 190-200°C for four hours in presence of 3-5 drops of concentrated sulphuric acid. The dye was isolated and purified in the similar way as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein, yield 1.8g.

The red crystalline dye decomposed at 224°C, is soluble in ethanol, methanol, acetone and acetic acid. Its ethanolic solution is brownish-red which turns into red on adding a drop of alkali.

Anal.for. : $C_{16}H_{14}NClO_5$ (Mol.wt. 335.5)

Calc. : C, 57.23; H, 4.17; N, 4.17; Cl, 10.58;

Found : C, 57.13; H, 4.14; N, 4.15; Cl, 10.53;

ACETYLATION OF (4-AMINO 3-CHLORO PHENYL) RESORCINOL SUCCIN-AS-EIN :

[(4-acetyl amino 3-chloro phenyl) diacetyl resorcinol succin-as-ein]

The dye (1.0g) and fused sodium acetate (3.0g) with 15ml of freshly distilled acetic anhydride were taken in 50ml round bottom flask fitted with an air condenser. The contents

were refluxed at 120-130°C for about four hours. The hot contents were then poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon a dark yellow solid mass settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallised from aqueous ethanol and little acetic acid. It was dried in an oven at 60°C and then over phosphorous pentaoxide under reduced pressure, yield 0.82g.

The acetylated product is light yellow, microcrystalline in nature, m.p. above 360°C. It is soluble in benzene, chloroform and acetic acid.

Anal.for. : $C_{22}H_{20}NClO_7$ or $C_{16}H_{11}NClO_4(CH_3CO)_3$ (Mol.wt.445.5)

Calc. : C, 59.26; H, 4.49; N, 3.14; Cl, 7.97; acetyl, 28.96;

Found : C, 59.15; H, 4.45; N, 3.11; Cl, 7.91; acetyl, 28.88;

BROMINATION OF (4-AMINO 3-CHLORO PHENYL) RESORCINOL
SUCCIN-AS-EIN :

[(4-amino 3-bromo 5-chloro phenyl) dibromo resorcinol
succin-as-ein]

The bromination, purification and crystallization of the dye (1.0g) was carried out exactly in the same manner as described in the bromination of (4-amino 3-chloro phenyl) resorcinol nitro phthal-as-ein (page 211), yield 0.90g.

The dark brown amorphous dye, m.p. 237-238°C, is soluble in ether, ethanol, methanol, acetone and chloroform.

Anal.for. : $C_{16}H_{11}NClBr_3O_4$ (Mol.wt. 556.5)

Calc. : Br, 43.13; Found : 43.06;

CAUSTIC POTASH TREATMENT OF (4-AMINO 3-CHLORO PHENYL)
RESORCINOL SUCCIN-AS-EIN :

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated on a sand bath with a few drops of water in order to make it paste. The dye (1.0g) was then added to it. The contents heated for about four hours till the red colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. The red residue (I) settled down on just neutralising the excess of alkali. It was filtered and washed well with water. The filtrate when acidified further by adding excess of dilute hydrochloric acid, gave white precipitate (II) which was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent a brownish-red residue (III) was obtained.

Identification of Residue (I) :

It was identified as the unreacted residual dye, giving all colour reactions of the dye itself and it was further confirmed by mixed melting point determination with the authentic sample of the dye.

Identification of Residue (II) :

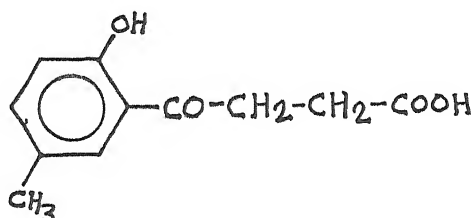
The compound, m.p. 122-124°C gave the usual tests of carboxylic and amino groups and was identified to be β -(4-amino 3-chloro benzoyl) propionic acid, and was confirmed by mixed melting point determination and superimposition of IR spectra with authentic sample.

Identification of Residue (III) :

The purified substance melted at 109-110°C. It gave blue violet colour with Ferric Chloride solution, reduced tollen's reagent and Fehling's solution. It responded to Fluorescein test with phthalic anhydride. On the basis of these observations the residue (III) was identified as resorcinol. It was further confirmed by mixed melting point determination with the authentic sample of resorcinol.

Acetylation, bromination and caustic potash fusion of the dye are shown in chart E (page 116).

2. DYES DERIVED FROM β -(2-HYDROXY 5-METHYL BENZOYL)
PROPIONIC ACID :



[β -(2-hydroxy 5-methyl benzoyl) propionic acid]

The acid was prepared by carrying out Friedel-Crafts reaction between p-cresol (dry AR 100ml) and succinic anhydride (10g about 0.1 mole) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole) in portions as catalyst. The yield of the acid was 17.5g. It was washed well with cold water dried and crystallised from acetone. The shining white crystals, m.p. 160-162°C, are soluble in water acetone and methanol.

Anal. for. : $C_{11}H_{12}O_4$ (Mol. wt. 208)

Calc. : C, 63.46; H, 5.77;

Found : C, 63.36; H, 5.74;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acid (1.0g) was acetylated and the product was isolated and purified exactly in similar manner as described in the case of acetylation of β -(4-amino 3-chloro benzoyl) propionic acid (page 233), yield 0.65g.

The blackish-brown diacetylated compound having m.p.

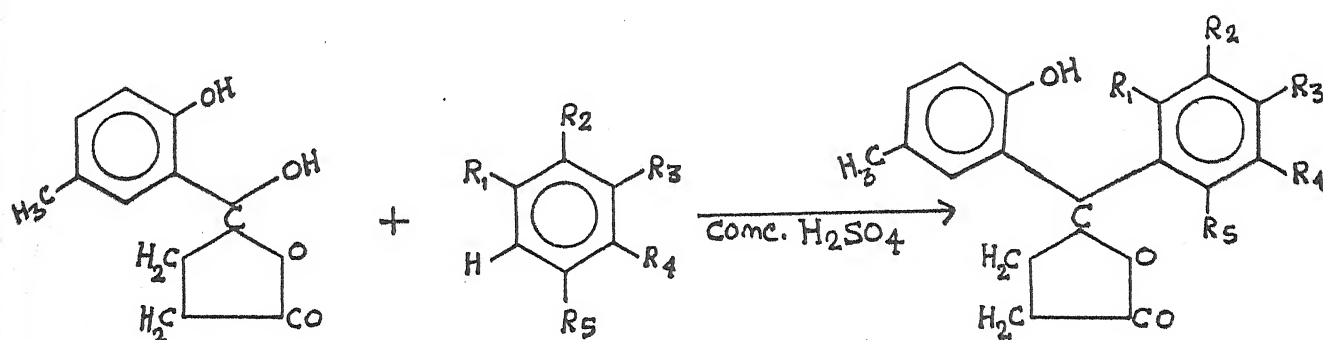
11-113°C, is soluble in acetone, chloroform and acetic acid.

Anal.for. : $C_{15}H_{16}O_6$ or $C_{11}H_{10}O_4(COCH_3)_2$ (Mol.wt.292)

Calc. : C, 61.64; H, 5.48; acetyl, 29.45;

Found : C, 61.55; H, 5.45; acetyl, 29.39;

The dyes prepared from the acid may be represented by the following structure:



Acid(Lactol form)

Phenolic compound.

Dye molecule.

(2-hydroxy 5-methyl phenyl) phenol succin-as-ein.

$R_1 = R_2 = R_4 = R_5 = H ; R_3 = OH$

(2-hydroxy 5-methyl phenyl) resorcinol succin-as-ein.

$R_2 = R_4 = R_5 = H ; R_1 = R_3 = OH$

(2-hydroxy 5-methyl phenyl) catechol succin-as-ein.

$R_3 = R_4 = R_5 = H ; R_1 = R_2 = OH$

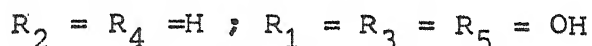
(2-hydroxy 5-methyl phenyl) hydroquinone succin-as-ein.

$R_2 = R_3 = R_5 = H ; R_1 = R_4 = OH$

(2-hydroxy 5-methyl phenyl) pyrogallol succin-as-ein.



(2-hydroxy 5-methyl phenyl) phloroglucinol succin-as-ein.



(2-acetoxy 5-methyl phenyl) diacetyl resorcinol succin-as-ein.



(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol succin-as-ein.



(2-HYDROXY 5-METHYL PHENYL) PHENOL SUCCIN-AS-EIN :

The dye was prepared by carrying out the condensation of the acid (1.5g) and phenol (1.0g) in an oil bath at 160-170°C for four hours, in presence of 3-4 drops of conc. sulphuric acid. The dye was isolated and purified in the same way as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235) yield 1.3g. The dark brown dye m.p. 135-137°C, gives light brown colour in ethanol which becomes deep on adding a drop of alkali.

Anal. for. : $C_{17}H_{16}O_4$ (Mol. wt. 284)

Calc. : C, 71.83; H, 5.63;

Found : C, 71.72; H, 5.60;

(2-HYDROXY 5-METHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

An intimate mixture of the acid (5.1g) and resorcinol

(3.0g) was heated in an oil bath at 120°C to make it homogeneous. Now 3-4 drops of conc. sulphuric acid were added and the contents were heated at $140-160^{\circ}\text{C}$ for four hours till the molten mass become hard and brittle on cooling. The isolation and purification of the dye were done in a similar manner as described in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 4.0g.

The brown shining dye having m.p. $216-217^{\circ}\text{C}$, is soluble in alcohol acetone and acetic acid. It gives light brown colour in ethanol which turns into reddish brown with green fluorescence on adding a drop of alkali. The colour becomes red with green fluorescence in strong alkaline medium.

Anal.for. : $\text{C}_{17}\text{H}_{16}\text{O}_5$ (Mol.wt. 300)

Calc. : C, 68.00; H, 5.33;

Found : C, 67.92; H, 5.30;

(2-HYDROXY 5-METHYL PHENYL) CATECHOL SUCCIN-AS-EIN :

The condensation of the intimate mixture of acid (2.5g) and catechol (1.5g) was carried out in presence of 2-3 drops of conc. sulphuric acid at $120-130^{\circ}\text{C}$ for three and half hours. Isolation and purification of the dye were done as in the cases of other dyes, yield 2.1g.

The brownish black dye, m.p. above 360°C , gives light brown colour with ethanol which become brown on adding a drop of alkali. It is soluble in alcohol acetone and acetic

acid.

Anal.for. : $C_{17}H_{16}O_5$ (Mol.wt. 300)

Calc. : C, 68.00; H, 5.33;

Found : C, 67.90; H, 5.29;

(2-HYDROXY 5-METHYL PHENYL) HYDROQUINONE SUCCIN-AS-EIN:

It is prepared by heating the homogeneous mixture of the acid (2.5g) and hydroquinone (1.5g) in an oil bath at $160-170^{\circ}C$ for four hours in presence of concentrated sulphuric acid. The dye was isolated and purified in the same way as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 2.0g.

The black shining crystalline dye decomposed at $210^{\circ}C$, gives light brown colour in ethanol which becomes brown on adding a drop of alkali.

Anal.for. : $C_{17}H_{16}O_5$ (Mol.wt. 300)

Calc. : C, 68.00; H, 5.33;

Found : C, 67.93; H, 5.28;

(2-HYDROXY 5-METHYL PHENYL) PYROGALLOL SUCCIN-AS-EIN :

The dye was prepared identically as described in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235). Acid (2.0g) and 2-3 drops conc. sulphuric acid were heated at $130-140^{\circ}C$ for about four hours, yield 2.5g.

The brownish-black dye having m.p. above 360°C , is soluble in ethanol, methanol, acetone and acetic acid. It gives golden brown colour in ethanol which turns into brown on adding a drop of alkali.

Anal.for. : $\text{C}_{17}\text{H}_{16}\text{O}_6$ (Mol.wt. 316)

Calc. : C, 64.56; H, 5.06;

Found : C, 64.46; H, 5.01;

(2-HYDROXY 5-METHYL PHENYL) PHLOROGLUCINOL SUCCIN-AS-EIN:

The mixture of acid (2.5g) phloroglucinol (1.5g) and 3.4 drops of conc. sulphuric acid, was heated in an oil bath at $190-210^{\circ}\text{C}$, for four hours. The isolation and purification were carried out in a same manner as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein, Yield 2.6g.

The red crystalline dye having m.p. $195-196^{\circ}\text{C}$, is soluble in acetone, ethanol, methanol and acetic acid. The ethanolic solution is orange-red in colour which changes to red on addition of a drop of alkali.

Anal.for. : $\text{C}_{17}\text{H}_{16}\text{O}_6$ (Mol.wt. 316)

Calc. : C, 64.56; H, 5.06;

Found : C, 64.48; H, 5.03;

ACETYLATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL SUCCIN-AS-EIN :

[(2-acetoxy 5-methyl phenyl) diacetyl resorcinol succin-as-ein]

The dye (2-hydroxy 5-methyl phenyl) resorcinol succin-

-as-ein (1.0g) was acetylated and the product was isolated and purified identically as the acetylation of (4-amino 3-chloro phenyl) resorcinol succin-as-ein (page 239), yield 0.60g.

The acetylated product was light yellow in colour, m.p. 235-236°C. It is soluble in benzene, ether, acetone, chloroform and acetic acid.

Anal.for. : $C_{23}H_{22}O_8$ or $C_{17}H_{13}O_5(COCH_3)_3$ (Mol.wt. 426)

Calc. : C, 64.79; H, 5.16; acetyl, 30.28;

Found : C, 64.70; H, 5.13; acetyl, 30.21;

BROMINATION OF (2-HYDROXY 5-METHYL PHENYL) RESORCINOL SUCCIN-AS-EIN :

[(3-bromo 2-hydroxy 5-methyl phenyl) dibromo resorcinol succin-as-ein]

The bromination, isolation and purification of the dye (1.0g) was carried out exactly in a same way as the bromination of (4-amino 3-chloro phenyl) resorcinol succin-as-ein (page 240), yield 0.85g.

The brown crystalline dye has m.p. 212-214°C. It is soluble in benzene, acetone, methanol and chloroform.

Anal.for. : $C_{17}H_{13}Br_3O_5$ (Mol.wt. 537)

Calc. : Br, 44.69; Found : Br, 44.60;

CAUSTIC POTASH TREATMENT OF (2-HYDROXY 5-METHYL PHENYL)
RESORCINOL SUCCIN-AS-EIN :

Caustic potash treatment of the dye (1.0g) was carried out in an identical manner as in the case of (4-amino 3-chloro phenyl) resorcinol succin-as-ein (page 241). As a result of fusion three residues were obtained.

Identification of Residue (I) :

It was identified and confirmed as the unreacted residual dye from its colour reactions and mixed melting point determination with the authentic sample of dye.

Identification of Residue (II) :

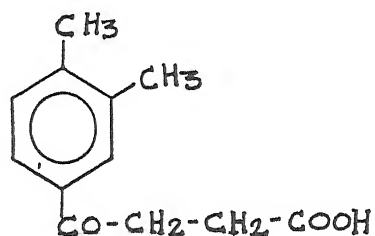
It was recrystallised from acetone/methanol, m.p. 160-162°C. It gave positive tests for carboxyl and phenolic groups and was identified and confirmed to be β -(2-hydroxy 5-methyl benzoyl) propionic acid from mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue (III) :

It was crystallised from ether. The compound, m.p. 110°C, gave violet blue colour with ferric chloride and reduced ammonical silver nitrate and Fehling's solution. The melting point did not depress when mixed with the authentic sample of resorcinol. Thus it was inferred to be resorcinol.

Caustic potash fusion, acetylation and bromination of resorcinol dye are shown in chart F (page 118).

3. DYES DERIVED FROM β -(3,4-DIMETHYL BENZOYL) PROPIONIC ACID:



β -(3,4-dimethyl benzoyl) propionic acid.

The acid was prepared by Friedel-Crafts reaction between orthoxylene (dry AR 80ml) and succinic anhydride (10.0g about 0.1 mole) in presence of anhydrous aluminium chloride (27.0g about 0.2 mole) as catalyst. The yield of the acid was 16.0g. It was washed well with cold water, dried and crystallised from benzene/petroleum ether. The white crystals, m.p. 98-99°C of the acid are soluble in benzene, ether, acetone and chloroform.

Anal. for. : $C_{12}H_{14}O_3$ (Mol. wt. 206)

Calc. : C, 69.90; H, 6.80;

Found : C, 69.81; H, 6.75;

PREPARATION OF ACETYL DERIVATIVE OF THE ACID :

The β -(3,4-dimethyl benzoyl) propionic acid (1.0g) was acetylated and the acetyl derivative was isolated and purified exactly in an identical manner as mentioned in the case of acetylation of β -(4-amino 3-chloro benzoyl) propionic acid, ^(page 233) yield 0.65g.

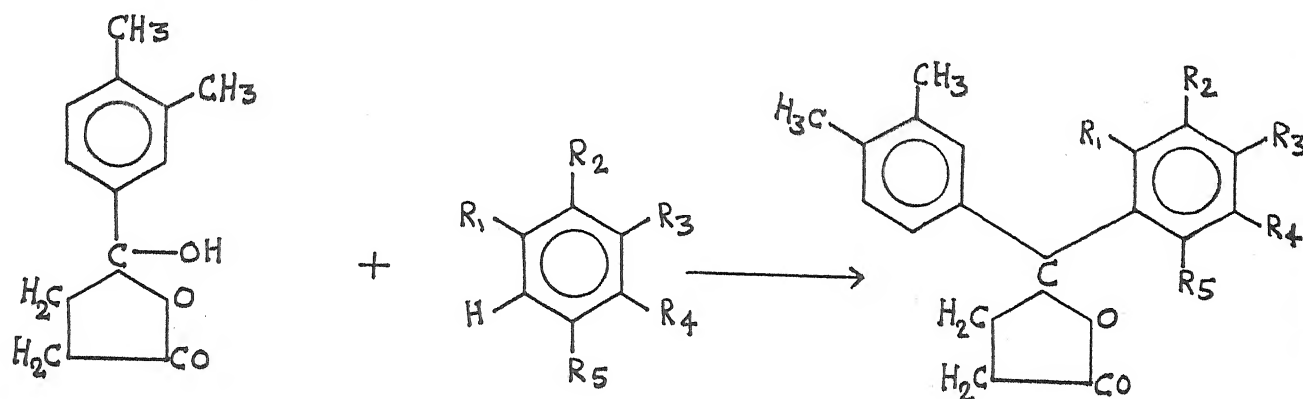
The blackish-brown diacetylated product has m.p. 90-91°C. It is soluble in alcohol, chloroform and acetic acid.

Anal.for. : $C_{14}H_{16}O_4$ or $C_{12}H_{13}O_3 (COCH_3)$ (Mol.wt. 284)

Calc. : C, 67.74; H, 6.45; acetyl, 17.34;

Found : C, 67.65; H, 6.41; acetyl, 17.28;

The dyes prepared from the acid may be represented by the following structures:



Acid
(Lactol form)

Phenolic
compound.

Dye
molecule.

(3,4-dimethyl phenyl) phenol succin-as-ein.

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

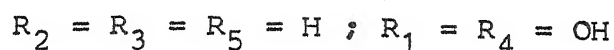
(3,4-dimethyl phenyl) resorcinol succin-as-ein.

$R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

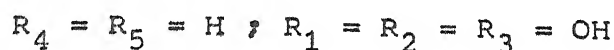
(3,4-dimethyl phenyl) catechol succin-as-ein.

$R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$

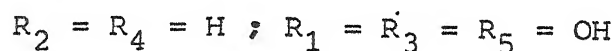
(3,4-dimethyl phenyl) hydroquinone succin-as-ein.



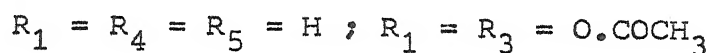
(3,4-dimethyl phenyl) pyrogallol succin-as-ein.



(3,4-dimethyl phenyl) phloroglucinol succin-as-ein.



(3,4-dimethyl phenyl) diacetyl resorcinol succin-as-ein.



(3,4-dimethyl phenyl) dibromo resorcinol succin-as-ein.



(3,4-DIMETHYL PHENYL) PHENOL SUCCIN-AS-EIN :

The dye was prepared by condensing the homogeneous mixture of the acid (2.0g) and phenol (1.5g) at 160-170°C for four hours in presence of 2-3 drops of conc.sulphuric acid. The isolation and purification was carried out in the same way as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 1.6g.

The dark brown dye having m.p. 140-142°C, dissolves in ethanol giving golden yellow colour, which turns into brown on adding a drop of alkali.

Anal.for. : $C_{18}H_{18}O_3$ (Mol.wt. 282)

Calc. : C, 76.60; H, 6.38;

Found : C, 76.49; H, 6.34;

(3,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

It was prepared by carrying out the condensation of the acid (5.0g) and resorcinol (2.9g) in an oil bath at 140-150°C for four hours, in presence of 5-6 drops of conc.sulphuric acid. The dye was isolated and purified in a similar manner as in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235), yield 4.2g.

The dark brown dye having m.p. 222-224°C, is soluble in benzene, chloroform, alcohol and acetic acid. It gives golden yellow colour in ethanol which changes into wine red with green fluorescence on adding a drop of alkali.

Anal.for. : $C_{18}H_{18}O_4$ (Mol.wt. 298)

Calc. : C, 72.48; H, 6.04;

Found : C, 72.40; H, 6.01;

(3,4-DIMETHYL PHENYL) CATECHOL SUCCIN-AS-EIN:

It was prepared by heating the intimate mixture of the acid (1.5g) and catechol (1.0g) in an oil bath at 120-130°C in presence of conc.sulphuric acid (2-3 drops) for about three hours. The isolation and purification were done in a similar manner as described in the case of (4-amino 3-chloro phenyl) catechol succin-as-ein (page 235), yield 1.3g.

The black coloured dye, m.p. above 360°C, gives light brown colour with ethanol which becomes dark on adding a drop of alkali.

Anal.for. : $C_{18}H_{18}O_4$ (Mol.wt. 298)

Calc. : C, 72.48; H, 6.04;

Found : C, 72.37; H, 6.02;

(3,4-DIMETHYL PHENYL) HYDROQUINONE SUCCIN-AS-EIN:

The mixture of the acid (2.5g) hydroquinone (1.5g) and few drops of conc.sulphuric acid, was heated in a oil bath at $160-180^{\circ}C$, for about three and half hours. The isolation and purification of the dye were carried out in a same manner as in the case of (4-amino 3-chloro phenyl) hydroquinone succin-as-ein (page 235), yield 3.2g.

The black dye having m.p. $220^{\circ}C$, gives light brown colour in ethanol which becomes dark on addition of alkali.

Anal.for. : $C_{18}H_{18}O_4$ (Mol.wt. 298)

Calc. : C, 72.48; H, 6.04;

Found : C, 72.39; H, 6.01;

(3,4-DIMETHYL PHENYL) PYROGALLOL SUCCIN-AS-EIN:

The condensation of the intimate mixture of acid (2.5g) pyrogallol (1.5g) was carried out in presence of 3-4 drops of conc.sulphuric acid at $130-140^{\circ}C$ for four hours. Isolation and purification of the dye were done as in the cases of other dyes, yield 2.8g.

The black coloured dye, m.p. above $360^{\circ}C$, is soluble

in acetone, ethanol, methanol and acetic acid. Its ethanolic solution is crimson which turns into dark red on adding a drop of alkali.

Anal.for. : $C_{18}H_{18}O_5$ (Mol.wt. 314)

Calc. : C, 68.79; H, 5.73;

Found : C, 68.72; H, 5.69;

(3,4-DIMETHYL PHENYL) PHLOROGLUCINOL SUCCIN-AS-EIN:

The dye was prepared isolated and purified identically as described in the case of (4-amino 3-chloro phenyl) phenol succin-as-ein (page 235). Acid (3.0g) phloroglucinol (1.5g) and (3-4) drops of conc. sulphuric acid were heated at 190-200°C for about four hours, yield 3.8g.

The dark brown dye decomposed at 180°C, is soluble in acetone, ethanol, methanol and acetic acid.

Anal.for. : $C_{18}H_{18}O_5$ (Mol.wt. 314)

Calc. : C, 68.79; H, 5.73;

Found : C, 68.69; H, 5.70;

ACETYLATION OF (3,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

[(3,4-dimethyl phenyl) diacetyl resorcinol succin-as-ein.]

The dye (3,4-dimethyl phenyl) resorcinol succin-as-ein (1.0g) was acetylated, isolated and purified identically in a similar manner as in the case of acetylation of (4-amino

3-chloro phenyl) resorcinol succin-as-ein (page 239), yield 0.68g.

The acetylated brown product having m.p. 310-312°C, is soluble in benzene, ether, acetone, chloroform and acetic acid.

Anal. for. : $C_{22}H_{22}O_6$ or $C_{18}H_{16}O_4(COCH_3)_2$ (Mol. wt. 382)

Calc. : C, 69.11; H, 5.76; acetyl, 22.51;

Found : C, 69.02; H, 5.72; acetyl, 22.45;

BROMINATION OF (3,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

[(3,4-dimethyl phenyl) dibromo resorcinol succin-as-ein]

The dye (3,4-dimethyl phenyl) resorcinol succin-as-ein (1.0g) was brominated and the product was extracted and purified in the similar way as described in the bromination of (4-amino 3-chloro phenyl) resorcinol succin-as-ein (page 244), yield 0.85g.

The dark brown dye, m.p. 150-151°C, is soluble in benzene, ether, acetone, methanol and chloroform.

Anal. for. : $C_{18}H_{16}Br_2O_4$ (Mol. wt. 456)

Calc. : Br, 35.09; Found : Br, 35.00;

CAUSTIC POTASH TREATMENT OF (3,4-DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN :

Potassium hydroxide fusion of the dye (1.0g) was carried out in a similar manner as in the case of (4-amino 3-chloro phenyl) resorcinol succin-as-eins (page 241). Following three residues obtained were identified.

Identification of Residue (I) :

Residue (I) was identified as unreacted residual dye from its colour reactions. It was further confirmed by mixed melting point determination with the original dye.

Identification of Residue (II) :

It was found to be acidic, m.p. $98-99^{\circ}\text{C}$, gave positive test for carboxylic acid and was identified to be β -(3,4-dimethyl benzoyl) propionic acid and confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Identification of Residue (III) :

The compound, m.p. 110°C gave violet blue colour with ferric chloride and responded fluorescein test with phthalic anhydride. It reduced Fehling's solution and Tollen's reagent. The melting point did not show any depression when mixed with the authentic sample of resorcinol. It was inferred to be resorcinol.

The acetylation, bromination and caustic potash fusion of the resorcinol dye are given in chart G (page 120).

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MELTING POINT, SHADE, COLOUR IN DIFFERENT MEDIUMS AND ABSORPTION MAXIMA OF THE DYES OBTAINED FROM DIFFERENT ACIDS DESCRIBED IN THE THESIS ARE GIVEN IN TABULAR FORM.

Note: G.F. = Green Fluorescence ; D = Decomposed.

- (A) λ -max of Phenolphthalein 550nm (alk.medium); Fluorescein 460nm (neutral medium), 500nm (alk.medium); Eosine 530nm (neutral and alkaline medium), were determined.
- (B) λ -max of Phthalein analogues of tetra chloro Phthalic anhydride:
Phenolphthalein analogues 585nm (alk.medium). Fluorescein analogue 470nm and 500nm (neutral medium), 520nm (alk. medium); Eosin analogue 520nm and 560nm (neutral medium), 550nm (alk.medium) were determined.
- (C) λ -max of Phthalein analogues of 3-Nitro Phthalic anhydride:
Phenolphthalein analogue, 560nm (alkaline medium); Fluorescein analogue, 480nm (neutral medium), 510nm (alkaline medium), Eosine analogue 530nm (neutral medium), 540nm (alkaline medium) were determined.
- (D) λ -max of Succinein analogues:
Fluorescein analogues, 480-485nm (neutral medium); 490-500nm (alkaline medium).

TABLE-I

DYES DERIVED FROM O-(4-AMINO 3-CHLORO BENZOYL) BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol Neutral Alkaline	Colour with 2% NaOH	λ -max (nm)	PH	Medium
Phenol	Buff	140-141°C	Brownish-red	Pink	520 530	6.5 9.8	Neu. Alk.
Resorcinol	Red	275-277°C	Golden Yellow(G.F)	Reddish-Yellow(G.F)	520 560	6.2 9.6	Neu. Alk.
Catechol	Black	>360°C	Brown	Brownish-black	-	-	Neu. Alk.
Hydroquinone	Black	>300°C (D)	Golden-brown	Leaf brown	-	-	Neu. Alk.
Pyrogallol	Black	300°C (D)	Wine red	Blue violet	-	-	Neu. Alk.
Phloroglucinol	Dark orange	>360°C	Golden yellow	Reddish orange	-	-	Neu. Alk.
Acetyl derivative of resorcinol	Light dye yellow	175-176°C	Light yellow	Greenish Yellow(G.F)	-	-	Neu. Alk.
Bromo derivative of resorcinol dye.	Pale orange	252-253°C	Pink(G.F)	Yellowish pink(G.F)	450 480	6.6 9.6	Neu. Alk.

TABLE-2

DYES DERIVED FROM O-(3-CARB METHOXY 4-HYDROXY BENZOYL) BENZOIC ACID

Phenol	Shade of dye	M.P.	Colour in ethanol Neutral	Colour in ethanol Alkaline	Colour with 2% NaOH	λ -max (nm)	PH	Medium
Phenol	Orange	126-127°C	Brownish red	Pink	Pink	460 500	6.5 9.5	Neu. Alk.
Resorcinol	Red	182-184°C	Golden yellow(G.F)	Reddish yellow(G.F)	Reddish yellow(G.F)	520 560	6.5 9.6	Neu. Alk.
Catechol	Black	>360°C	Brown	Brownish black	Brownish black	- -	- -	Neu. Alk.
Hydroquinone	Black	>300°C(D)	Crimson (Light brown)	Brown	Brown	- -	- -	Neu. Alk.
Pyrogallol	Black	>320°C	Wine red	Blue violet	Blue violet	- -	- -	Neu. Alk.
Phloroglucinol	Dark orange	>360°C	Golden yellow	Reddish orange	Reddish orange	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye	Light yellow	200-202°C	Light yellow(G.F)	Bright yellow(G.F)	Bright yellow(G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye	Pale yellow	256-257°C	Orange	Yellowish pink(G.F)	Yellowish pink(G.F)	450 480	6.5 9.6	Neu. Alk.

TABLE-3

DYES DERIVED FROM O-(2-HYDROXY 5-METHYL BENZOYL) BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Pinkish red	138-139°C	Light yellow	Pink	Pink	510 530	6.0 9.5	Neu. Alk.
Resorcinol	Dark orange	290-292°C	Golden yellow(G.F)	Reddish yellow(G.F)	Reddish yellow(G.F)	460 510	6.5 9.5	Neu. Alk.
Catechol	Black	>360°C	Brown	Brownish black	Brownish black	- -	- -	Neu. Alk.
Hydroquinone	Black	320°C(D)	Crimson	Dark brown	Dark brown	- -	- -	Neu. Alk.
Pyrogallol	Black	>360°C	Wine red	Blue violet	Blue violet	- -	- -	Neu. Alk.
Phloroglucinol	Orange	320-322°C	Yellow	Dark red	Dark red	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye.	Yellow	188-190°C	Light yellow	Yellow (G.F)	Yellow(G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye.	Orange	250-251°C	Orange	Reddish pink(G.F)	Reddish pink(G.F)	460 500	6.2 9.0	Neu. Alk.

TABLE-4

DYES DERIVED FROM O-(3,4-DIMETHYL BENZOYL) BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Brown	178-180°C	Light yellow	Pink	Pink	520 535	6.5 9.2	Neu. Alk.
Resorcinol	Orangish yellow	155-157°C	Yellow(G.F)	Brownish yellow(G.F)	Brownish yellow(G.F)	430 480	6.5 9.0	Neu. Alk.
Catechol	Black	>360°C	Light brown	Dark black	Black	- -	- -	Neu. Alk.
Hydroquinone	Black	>360°C	Golden brown	Dark brown	Dark brown	- -	- -	Neu. Alk.
Pyrogallol	Black	>360°C	Wine red	Violet	Violet	- -	- -	Neu. Alk.-
Phloroglucinol	Dark brown	>360°C(D)	Lemon yellow	Orange	Orange	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye	Light dye	110-112°C	Light yellow	Reddish yellow(G.F)	Reddish yellow(G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye	Dirty orange	88-89°C	Light orange	Yellowish orange(G.F)	Yellowish orange(G.F)	450 490	6.0 9.0	Neu. Alk.

TABLE-5

DYES DERIVED FROM O-(4-AMINO 3-CHLORO BENZOYL) TETRA CHLORO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol Neutral	Alkaline	Colour with 2% NaOH	λ -max (nm)	PH	Medium
Phenol	Orangish brown	258-260°C	Light yellow	Violet	Violet	490 520	6.5 9.5	Neu. Alk.
Resorcinol	Lemon yellow	290-292°C	Pale cream	Light orange(G.F)	Light orange(G.F)	450 500	6.2 9.5	Neu. Alk.
Catechol	Black	250°C(D)	Light brown	Golden brown	Golden brown	- -	- -	Neu. Alk.
Hydroquinone	Black	300°C(D)	Golden brown	Yellowish brown	Yellowish brown	- -	- -	Neu. Alk.
Pyrogallol	Black	180°C(D)	Brown	Blackish brown	Blackish brown	- -	- -	Neu. Alk.
Phloroglucinol	Grey	300°C(D)	Grey	Pale cream	Pale cream	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye.	Buff	180-182°C	Light brown	Yellowish pink(G.F)	Yellowish pink	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye.	Grey	155-157°C	Light pink	Deep pink	Deep pink	500 520	6.5 9.2	Neu. Alk.

TABLE-6

DYES DERIVED FROM O-(3-CARBOMETHOXY 4-HYDROXY BENZOYL) TETRA CHLORO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol Neutral Alkaline	Colour with 2% NaOH	λ -max (nm)	PH	Medium
Phenol	Orange	240-242°C	Golden yellow	Violet	460 500	6.8 9.2	Neu. Alk.
Resorcinol	Light brown	280-282°C	Pale yellow	Reddish orange(G.F)	510 530	6.5 9.5	Neu. Alk.
Catechol	Light black	240-241°C	Brown	Blackish brown	-	-	Neu. Alk.
Hydroquinone	Black	300°C(D)	Light brown	Dark brown	-	-	Neu. Alk.
Pyrogallol	Brown	> 360°C	Wine red	Blue	-	-	Neu. Alk.
Phicroglucinol	Dark orange	300°C(D)	Wine red	Red(G.F)	-	-	Neu. Alk.
Acetyl derivative of resorcinol dye brown	Golden	166-168°C	Light pink	Pink(G.F)	-	-	Neu. Alk.
Bromo derivative of resorcinol dye yellow	Pale	308-309°C	Pinkish orange	Dark pink (G.F)	440 460	6.5 9.5	Neu. Alk.

TABLE-7

DYES DERIVED FROM O-(2-HYDROXY-5-METHYL BENZOYL) TETRA CHLORO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Reddish orange	220-222°C	Light yellow	Violet	Violet	480 520	6.5 9.2	Neu. Alk.
Resorcinol	Greenish brown	280-281°C	Cream	Reddish orange(G.F)	Reddish orange(G.F)	430 510	6.5 9.5	Neu. Alk.
Catechol	Black	242-243°C	Golden brown	Brown	Brown	- -	- -	Neu. Alk.
Hydroquinone	Black	270°C(D)	Light brown	Brown	Brown	- -	- -	Neu. Alk.
Pyrogallol	Black	>360°C	Dark brown	Blue	Blue	- -	- -	Neu. Alk.
Phloroglucinol	Dark red	180°C(D)	Wine red	Red(G.F)	Red(G.F)	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye.	Golden brown	165-167°C	Light brown	Pink(G.F)	Pink(G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye.	Brownish cream	315-317°C	Light pink	Dark pink	Dark pink	510 530	6.8 9.5	Neu. Alk.

TABLE-8

DYES DERIVED FROM O-(3,4-DIMETHYL BENZOYL) TETRA CHLORO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Pink	232-234°C	Wine red	Violet	Violet	530 560	6.8 9.5	Neu. Alk.
Resorcinol	Golden brown	281-283°C	Pale cream	Pinkish orange (G.F)	Pinkish orange (G.F)	510 530	6.5 9.6	Neu. Alk.
Catechol	Black	243-245°C	Brown	Brown	Brown	- -	- -	Neu. Alk.
Hydroquinone	Light black	320°C(D)	Golden brown	Golden brown	Brown	- -	- -	Neu. Alk.
Pyrogallol	Blackish brown	>360°C	Golden brown	Dark brown	Dark brown	- -	- -	Neu. Alk.
Phloroglucinol	Dark orange	240°C	Wine red	Dark red	Dark red	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye	Buff	310-312°C	Light brown	Pink (G.F)	Pink (G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye	Pale yellow	120-121°C	Yellowish pink	Pink	Pink	440 460	6.6 9.5	Neu. Alk.

TABLE-9

DYES DERIVED FROM O-(4-AMINO 3-CHLORO BENZOYL) m-NITRO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Blackish brown	300°C(D)	Brown	Reddish violet	Reddish violet	520 545	6.8 9.6	Neu. Alk.
Resorcinol	Greenish brown	312°C(D)	Lemon yellow	Red (G.F)	Red (G.F)	430 510	6.6 9.5	Neu. Alk.
Catechol	Black	>360°C	Brown	Brownish black	Brownish black	-	-	Neu. Alk.
Hydroquinone	Black	234°C	Light brown	Dark brown	Dark brown	-	-	Neu. Alk.
Pyrogallol	Black	>360°C	Light brown	Brown	Brown	-	-	Neu. Alk.
Phloroglucinol	Brownish red	320°C(D)	Orangish red	Orange red	Orange red	-	-	Neu. Alk.
Acetyl derivative of resorcinol dye	Buff	280°C(D)	Brown	Reddish brown (G.F)	Reddish brown (G.F)	-	-	Neu. Alk.
Bromo derivative of resorcinol dye	Dark brown	182°C(D)	Brown	Dark red	Dark red	520 545	6.8 9.6	Neu. Alk.

TABLE-10

DYES DERIVED FROM O-(4-HYDROXY 5-METHYL BENZOYL) m-NITRO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Neutral	Colour in ethanol	Alkaline	Colour with 2% NaOH	λ -max (nm)	PH	Medium
Phenol	Brown	>360°C	Light brown	Light pink		Pink	520 535	6.2 9.5	Neu. Alk.
Resorcinol	Brown	301-303°C	Light yellow	Brownish red (G.F)		Brownish red (G.F)	520 540	6.5 9.6	Neu. Alk.
Catechol	Brownish black	>360°C	Light brown	Brown		Brown	- -	- -	Neu. Alk.
Hydroquinone	Black	262°C(D)	Light brown	Brown		Brown	- -	- -	Neu. Alk.
Pyrogallol	Brownish black	>360°C	Light brown	Brown		Brown	- -	- -	Neu. Alk.
Phloroglucinol	Red	>360°C	Wine red	Orangish red		Orangish red	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye	Light yellow	242°C	Light brown	Brown (G.F)		Brown (G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye	Brown	174°C	Brown	Dark red		Dark red	520 545	6.8 9.5	Neu. Alk.

TABLE-11

DYES DERIVED FROM O-(3,4-DIMETHYL BENZOYL) m-NITRO BENZOIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Light brown	>360°C	Light brown	Light violet	Violet	510 530	6.2 9.5	Neu. Alk.
Resorcinol	Brown	284-286°C	Brown	Brownish red (G.F)	Brownish red (G.F)	520 540	6.5 9.6	Neu. Alk.
Catechol	Black	>360°C	Black	Blackish brown	Blackish brown	- -	- -	Neu. Alk.
Hydroquinone	Black	210°C(D)	Light brown	Dark brown	Dark brown	- -	- -	Neu. Alk.
Pyrogallol	Black	>360°C	Light brown	Brown	Brown	- -	- -	Neu. Alk.
Phloroglucinol	Brownish red	339-340°C	Brown	Red	Red	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye	Yellow	235-236°C	Brown	Reddish brown	Reddish brown	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye	Dark brown	212-213°C	Brown	Red	Red	520 545	6.5 9.8	Neu. Alk.

TABLE-12

DYES DERIVED FROM β -(4-AMINO 3-CHLORO BENZOYL) PROPIONIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ_{max} (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Brown	110-111°C	Light brown	Brown	Brown	520 540	6.8 9.8	Neu. Alk.
Resorcinol	Orange	207-209°C	Wine red	Reddish orange (G.F)	Reddish brown (G.F)	460 500	6.5 9.5	Neu. Alk.
Catechol	Black	>360°C	Light brown	Brown	Brown	- -	- -	Neu. Alk.
Hydroquinone	Brown	250°C(D)	Light brown	Brown	Brown	- -	- -	Neu. Alk.
Pyrogallol	Black	>360°C	Light brown	Brown	Brown	- -	- -	Neu. Alk.
Phloroglucinol	Red	224°C(D)	Brownish red	Red	Red	- -	- -	Neu. Alk.
Acetyl derivative of resorcinol dye	Light yellow	>360°C	Light yellow	Wine red (G.F)	Wine red (G.F)	- -	- -	Neu. Alk.
Bromo derivative of resorcinol dye	Dark brown	237-238°C	Pink	Pink	Pink	520 545	6.2 9.8	Neu. Alk.

TABLE-13

DYES DERIVED FROM β - (2-HYDROXY 5-METHYL BENZOYL) PROPIONIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Dark brown	135-137°C	Light brown	Brown	Brown	520 545	6.6 9.5	Neu. Alk.
Resorcinol	Brown	216-217°C	Light brown	Reddish brown (G.F)	Reddish brown (G.F)	510 530	6.5 9.4	Neu. Alk.
Catechol	Brownish black	>360°C	Light brown	Brown	Brown	-	-	Neu. Alk.
Hydroquinone	Black	210°C (D)	Light brown	Brown	Brown	-	-	Neu. Alk.
Pyrogallol	Brownish black	>360°C	Golden brown	Brown	Brown	-	-	Neu. Alk.
Phloroglucinol	Red	195-196°C	Orange red	Red	Red	-	-	Neu. Alk.
Acetyl derivative of resorcinol dye	Light yellow	335-336°C	Yellow	Wine red	Red	-	-	Neu. Alk.
Bromo derivative of resorcinol dye	Brown	212-214°C	Light pink	Dark pink	Dark pink	510 535	6.6 9.6	Neu. Alk.

TABLE-14

DYES DERIVED FROM β -(3,4-DIMETHYL BENZOYL) PROPIONIC ACID.

Phenol	Shade of dye	M.P.	Colour in ethanol		Colour with 2% NaOH	λ -max (nm)	PH	Medium
			Neutral	Alkaline				
Phenol	Dark brown	140-142°C	Golden yellow	Brown	Brown	520 545	6.5 9.5	Neu. Alk.
Resorcinol	Dark brown	222-224°C	Golden yellow	Wine red (G.F)	Wine red (G.F)	510 545	6.8 9.6	Neu. Alk.
Catechol	Black	>360°C	Golden brown	Dark brown	Dark brown	-	-	Neu. Alk.
Hydroquinone	Black	220°C	Light brown	Dark brown	Dark brown	-	-	Neu. Alk.
Pyrogallol	Black	>360°C	Crimson	Dark red	Dark red	-	-	Neu. Alk.
Phloroglucinol	Dark brown	180°C(D)	Wine red	Wine red	Red	-	-	Neu. Alk.
Acetyl derivative of resorcinol dye	Brown	310-312°C	Brown	Wine red	Wine red	-	-	Neu. Alk.
Bromo derivative of resorcinol dye	Dark brown	150-151°C	Brown	Dark brown	Dark brown	520 540	6.8 9.5	Neu. Alk.